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Effects of Mg$_{2.05}$SiO$_{4.05}$ addition on phase structure and microwave properties of MgTiO$_3$–CaTiO$_3$ ceramic system

Hao Li*, Bin Tang*, Yingxiang Li, Zhenjun Qing, Shuren Zhang

National Engineering Research Center of Electromagnetic Radiation Control Materials, University of Electronic Science and Technology of China, Chengdu 610054, China

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ABSTRACT

The $(1-x)$ MgTiO3$-x$Mg$_{2.05}$SiO$_{4.05}$–0.06CaTiO$_3$ ceramic system composite dielectric ceramics with different amounts of Mg$_{2.05}$SiO$_{4.05}$ addition were prepared by solid state reaction method. The results indicated that exceeding Mg in Mg$_{2.05}$SiO$_{4.05}$ not only hold back the formation of MgSiO$_3$ but also inhibits the formation of second phase MgTi$_2$O$_5$. A new microwave dielectric material, 0.8MgTiO$_3$–0.2Mg$_{2.05}$SiO$_{4.05}$–0.06CaTiO$_3$ ceramics sintered at 1380 °C for 4 h had optimal dielectric properties ($\varepsilon_r=15.4$, $Q\times f=72{,}705$ GHz and $\tau_f=-1.45$ ppm/°C) which satisfied microwave applications in resonators, filters and antenna substrates.

1. Introduction

Microwave dielectric materials play a key role in global society with a wide range of applications from terrestrial and satellite communication including software radio, GPS, and DBS TV to environmental monitoring via satellites [1]. The important characteristics required for a dielectric material used in millimeter-wave telecommunication systems are: (a) high dielectric constant (ε_r); (b) low dielectric loss (tanδ) and (c) low temperature coefficient of resonant frequency (τ_f).

MgTiO$_3$ has an ilmenite-type structure with $\varepsilon_r=17$, $Q\times f=160{,}000$ GHz at 7 GHz and $\tau_f=-50$ ppm/°C. Mg$_2$TiO$_4$ ceramic has a spinel structure and Belous et al. first reported its microwave dielectric properties ($\varepsilon_r=14$, $Q\times f=150{,}000$ GHz, and $\tau_f=-50$ ppm/°C) [2]. When MgO and TiO$_2$ are reacted with a stoichiometric ratio 1:1, the MgTi$_2$O$_5$ phase, having a much lower $Q\times f$ ($\sim$47,000 GHz) associated with an ε_r of 17.4 and a τ_f of -66 ppm/°C, was formed as an intermediate phase and is difficult to completely eliminate from the MgTiO$_3$ sample prepared by the mixed oxide route [3].

Tsunooka et al. [4] reported that forsterite (Mg$_2$SiO$_4$) show excellent microwave dielectric properties ($\varepsilon_r=6.8$, $Q\times f=270{,}000$ GHz, and $\tau_f=-67$ ppm/°C). However, the synthesis of a homogeneous Mg$_2$SiO$_4$ ceramic is known to be difficult because of the presence of the MgSiO$_3$ secondary phase, which is formed easily during the sintering of Mg$_2$SiO$_4$ ceramics. Song et al. [5] reported that the appearance of a MgSiO$_3$ secondary phase could be effectively suppressed by adjusting the nonstoichiometric, and a single-phase forsterite structure was obtained in the present ceramics with Mg/Si ratios of 2.05.

In order to obtain a kind of MgTiO$_3$–CaTiO$_3$ ceramic with $\varepsilon_r=10$–17 and low dielectric loss, $(1-x)$ MgTiO3–xMg$_{2.05}$SiO$_{4.05}$–0.06CaTiO$_3$ composite dielectric ceramics were prepared and characterized, and the effects of Mg$_{2.05}$SiO$_{4.05}$ addition amount on the microstructure and dielectric properties as well as the sintering temperature of ceramics were investigated.

2. Experimental procedures

The samples were separately by conventional solid-state method from individual high-purity oxide powders (>99.9%): MgCO$_3$, SiO$_2$, CaCO$_3$, and TiO$_2$. The starting materials were mixed according to the desired stoichiometry Mg$_{2.05}$SiO$_{4.05}$, MgTiO$_3$ and CaTiO$_3$. The powders were grounding distilled water for 12 h in a ball mill with agate balls. The mixtures of Mg$_{2.05}$SiO$_{4.05}$, MgTiO$_3$ and CaTiO$_3$ powders were dried and calcined at 1250 °C, 1150 °C and 1150 °C, respectively, for 3 h in air. After calcinations, the calcined powders were mixed according to the molar fraction $(1-x)$ MgTiO$_3$–xMg$_{2.05}$SiO$_{4.05}$–0.06CaTiO$_3$ ($x=0$, 0.2, 0.4, 0.6, 0.8) and then re-milled for 12 h. The fine powder with 3 wt% of a 10% solution of PVA as a binder was pressed into pellets with dimensions of 15 mm in diameter and 7.5 mm in thickness under the pressure of 200 kg/cm^2. These pellets were sintered at temperatures of 1330–1450 °C for 4 h in air.

The bulk densities of the sintered samples were measured by the Archimedes method. The phase composition was identified by X-ray diffraction (XRD) using Cu Kα radiation (Philips x'pert Pro MPD, Netherlands). Microstructure observation was conducted on the surface of samples by using scanning electron microscopy

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* Corresponding authors. Tel.: +86 28 8320 8048; fax: +86 28 83202139.
E-mail addresses: haouestc@gmail.com (H. Li), tangbin@uestc.edu.cn (B. Tang).

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(SEM, FEI Inspect F). The dielectric characteristics at microwave frequencies were measured by the Hakki–Coleman dielectric resonator method in the TE011 mode using a network analyzer (Agilent Technologies E5071C, the United States). [12] The temperature coefficient of resonant frequency (τ_f) was determined from the difference between the resonant frequency obtained at 25 °C and 85 °C using the equation: $\tau_f = (f_{t_2} - f_{t_1})/(f_{t_1} \times (t_2 - t_1))$, where f_{t_1} and f_{t_2} are the resonant frequencies at $t_1 = 25$ °C and $t_2 = 85$ °C, respectively.

3. Results and discussion

$MgSiO_3$ was difficult to eliminate according to stoichiometric solid-phase sintering methods. [6] Fig. 1(a) shows the XRD patterns of $Mg_{2.05}SiO_{4.05}$ powders calcined at 1250 °C in air for 3 h. An MgO secondary phase was detected in the powders and protoenstatile $MgSiO_3$ was not found. These results are consistent with those of Song [5]. Fig. 1(b) shows the XRD patterns of $0.94MgTiO_3$–$0.06CaTiO_3$ ceramic system sintered at 1380 °C for 4 h. It givens mixed phase of $MgTiO_3$ phase as the main phase associated with $CaTiO_3$. Moreover, a second $MgTi_2O_5$ was also detected, which would lead to a degradation in dielectric properties. It was attributed to that $MgTi_2O_5$ is usually formed as an intermediate phase and is difficult to eliminate completely from the sample when MgO and TiO_2 reacts in a 1:1 molar ratio.

Fig. 1(c) shows the XRD patterns of $MgTiO_3$–$xMg_{2.05}SiO_{4.05}$–$0.06CaTiO_3$ ($x=0.2$, 0.4, 0.6, 0.8) ceramics sintered at 1380 °C. It can be seen that the major phases of ceramics were $MgTiO_3$, Mg_2TiO_4, Mg_2SiO_4 and $CaTiO_3$, and no $MgTi_2O_5$, $MgSiO_3$ and MgO were detected. The reflection peaks of Mg_2SiO_4 phase and Mg_2TiO_4 phase tend to higher with increasing the x value, however, the reflection peaks of the $MgTiO_3$ phase tend to lower. When $x=0.8$, $MgTiO_3$ was not found. Exceeding Mg will hold back the formation of $MgTi_2O_5$ and Mg-rich cause the formation of Mg_2TiO_4 phase. The reaction can be expressed as follows:

$$MgTi_2O_5 + MgO \rightarrow MgTiO_3 \quad (1)$$

$$MgTiO_3 + MgO \rightarrow Mg_2TiO_4 \quad (2)$$

Fig. 2 shows the SEM photographs for $MgTiO_3$–$xMg_{2.05}SiO_{4.05}$–$0.06CaTiO_3$ ceramics with (a) $x=0.2$, (b) $x=0.4$, (c) $x=0.6$ and (d) $x=0.8$ sintered at 1380 °C for 4 h. Dense forsterite ceramics have been reported as being hard to obtain [6], and the poor sinter ability is considered to be due to the presence of $MgSiO_3$ and MgO secondary phases. In the present work, however, good densification is achieved in nonstoichiometric forsterite Mg_2SiO_4 ceramics, and a fine-grain structure is obtained.

For further determining the distribution of the elements, the energy dispersive X-ray analysis (EDX) was used in Fig. 2. According to the quantitative analysis as shown in Table 1, it is evident that the grains of A is $MgTiO_3$, B is Mg_2TiO_4, C is Mg_2SiO_4 and D is $CaTiO_3$. The mixture phases observed in the microstructure supported the phases composition detected in the X-ray diffraction patterns as shown in Fig. 1(c).

The apparent density of $MgTiO_3$–$xMg_{2.05}SiO_{4.05}$–$0.06CaTiO_3$ ceramics sintered at 1380 °C for 4 h is shown in Fig. 3(a). There was a steady decrease in the apparent density of samples when x was increased from 0 to 0.8 and it was because Mg_2SiO_4 (3.21 g/cm^3) and Mg_2TiO_4 (3.54 g/cm^3) with lower density than $MgTiO_3$ (3.89 g/cm^3) appeared more and more in the system. For the dielectric constant (ε_r) as shown in Fig. 3(b), it constantly dropped from 21.7 to 9.1 because Mg_2SiO_4 ($\varepsilon_r = 6.8$) and Mg_2TiO_4 ($\varepsilon_r = 14$) with a lower ε_r than $MgTiO_3$ ($\varepsilon_r = 16$) became more and more in the system. As shown in Fig. 3(c), the quality factor values only increased from 58,761 GHz to 76,789 GHz while x was varying from 0 to 0.6, and thereafter, the quality factor values started to decline to 73,136 GHz at $x=0.8$. The increase of $Q \times f$ value should be mainly attributed to increase of high $Q \times f$ value phase Mg_2SiO_4 (270,000 GHz), but the decrease might be related to the increase of Mg_2TiO_4 phase which need more high sintering

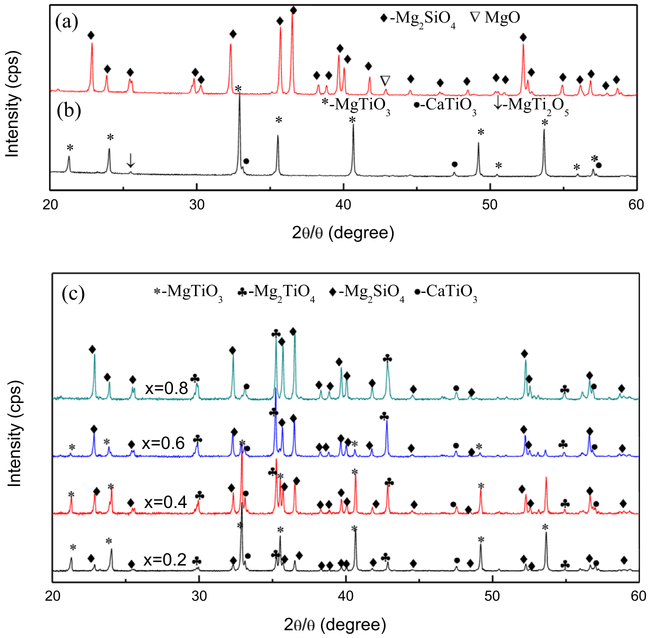

Fig. 1. Shows the XRD patterns of (a) $Mg_{2.05}SiO_{4.05}$ powders calcined at 1250 °C in air for 3 h, (b) $0.94MgTiO_3$–$0.06CaTiO_3$ sintered at 1380° °C for 4 h, (c) $(1-x)$ $MgTiO_3$–$xMg_{2.05}SiO_{4.05}$–$0.06CaTiO_3$ ($x=0.2$, 0.4, 0.6, 0.8) ceramics sintered at 1380° °C.

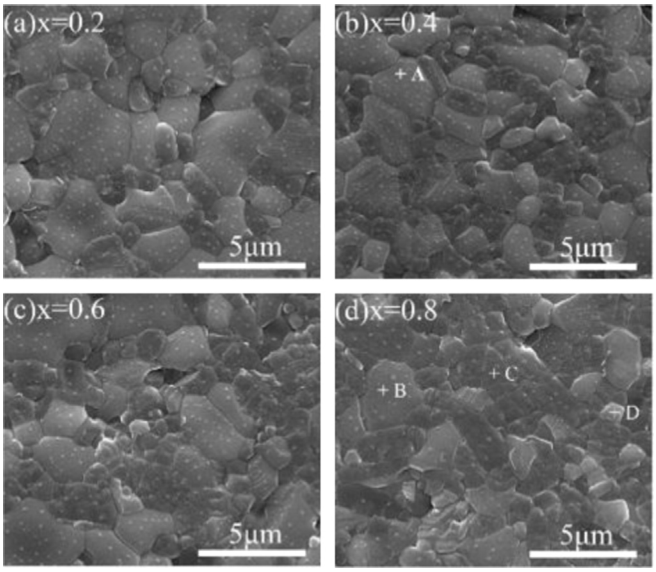

Fig. 2. Shows the SEM photographs for $(1-x)$ MgTiO3–$xMg_{2.05}SiO_{4.05}$–$0.06CaTiO_3$ ceramics with (a) $x=0.2$, (b) $x=0.4$, (c) $x=0.6$ and (d) $x=0.8$ sintered at 1380° °C for 4 h.

Table 1
The energy dispersive X-ray analysis (EDX) data of ceramics corresponding to Fig. 2.

Spot	Mg (at%)	Si (at%)	Ca (at%)	Ti (at%)	O (at%)
A	33.34	0	0	30.03	36.34
B	42.94	0	0	24.71	32.95
C	39.38	18.12	0	0	42.37
D	3.68	0	22.49	22.96	50.87