Available online at www.sciencedirect.com

ScienceDirect

ELSEVIER

Journal of the European Ceramic Society 28 (2008) 605–609

www.elsevier.com/locate/jeurceramsoc

A new microwave ceramic with low-permittivity for LTCC applications

Qi-Long Zhang*, Hui Yang, Hui-Ping Sun

College of Materials Science and Chemical Engineering, Zhejiang University, Hangzhou 310027, China

Received 18 April 2007; received in revised form 10 July 2007; accepted 14 July 2007
Available online 7 September 2007

Abstract

A new low-temperature microwave dielectric ceramic with low-permittivity was found and investigated in the CaO–MgO–SiO_2–TiO_2 system. Phase constitutes and dielectric properties of $(Ca_{1-x},Mg_x)SiO_3$ ($x = 0.1$–0.5) ceramics were studied with different x contents, and $CaTiO_3$ demonstrated an effective compensation in $(Ca_{1-x},Mg_x)SiO_3$ τ_f value. The $0.88CaMgSi_2O_6$–$0.12CaTiO_3$ compositions show a relatively low-permittivity (∼9.42), high $Q \times f$ values up to 52,800 GHz, and near-zero temperature coefficients (5.6 ppm/°C), which were obtained via sintering at 1300 °C. The addition of ≤2.0 wt% Li_2CO_3–V_2O_5 was very effective in lowering the sintering temperature (T_s), and dense ceramics could be obtained at $T_s \le 900$ °C. The addition of Li_2CO_3–V_2O_5 does not induce apparent degradation in the microwave properties. The specimens with 1 wt% Li_2CO_3–V_2O_5 sintered at 880 °C for 2 h shows excellent dielectric properties: $\varepsilon_r = 9.23$, $Q \times f = 46{,}200$ GHz, and $\tau_f = 1.3$ ppm/°C. The low-temperature sintering ceramics powders were suitable for the tape casting process. Also, the material is compatible with Ag electrodes, and therefore, is suitable for LTCC application.

Keywords: Dielectric properties; Microwave ceramic; (Ca, Mg)SiO_3; Li_2CO_3; LTCC

1. Introduction

The rapid growth of the telecommunication and satellite broadcasting industry has created a high demand for microwave ceramic components. Many materials have been developed and modified, according to the needs of the specific applications. Recently, considerable attention has been paid to the development of the low-temperature co-fired ceramics (LTCC) for the benefits offered for the fabrication of miniature multilayer devices. Several LTCC microwave dielectric ceramics systems such as $BiNbO_4$, $MTiO_3$ (M = Mg, Zn, Ca), BaO–TiO_2, $ZnNb_2O_6$, $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$, BaO–$R_2O_3$–$TiO_2$ (R = Nd, Sm), $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$, etc., have been developed over the years.[1–12] However, most of the reported LTCC microwave dielectric ceramics show relatively higher dielectric constant (>18), usually applied in low frequency ranges such as 1.89 and 2.45 GHz. Comparatively, LTCC microwave dielectric ceramics with low-permittivity, which are required for multilayer components particularly antennas and baluns working at a higher frequency such as 5.8 GHz, have not been extensively studied. Umemura et al.[13,14] reported the dielectric properties of solid solutions in the system $(Mg_{3-x}Co_x)(VO_4)_2$. $MgCo_2(VO_4)_2$ ceramics sintered 950 °C for 5 h has $\varepsilon_r = 9.5$, $Q \times f = 78{,}906$ GHz, and $\tau_f = -94.5$ ppm/°C. Bian et al.[15] conducted a detailed investigation on the dielectric properties of AMP_2O_7 (A = Ca, Sr; M = Zn, Cu). $SrZnP_2O_7$ has $\varepsilon_r = 7.06$, $Q \times f = 52{,}781$ GHz, and $\tau_f = -70$ ppm/°C. Although the two LTCC materials have relatively low-permittivity and high $Q \times f$ values, the high coefficient of temperature resonant frequency places a constraint on their manufacture for use in practical applications. Jantunen et al.[16] reported that $MgTiO_3$–$CaTiO_3$ ceramic with a large number of ZnO–B_2O_3–SiO_2 glasses sintered at 875 °C has $\varepsilon_r = 10.6$, and $Q \times f = 7000$ GHz. Recently, Kim et al.[17] acquired a new LTCC ceramics of $CaWO_4$ ($\varepsilon_r = 8.7$, $Q \times f = 70{,}220$ GHz, and $\tau_f = -15$ ppm/°C). However, the material price is too high. Moreover, many kinds of LTCC materials with low-permittivity have been developed in the form of glass + ceramics (multiphase ceramics)[18–21] and glass–ceramics (crystallizable glass).[22–25] Typical glass + ceramics systems include the

---

* Corresponding author. Tel.: +86 571 87953313; fax: +86 571 87953313.
E-mail address: mse237@zju.edu.cn (Q.-L. Zhang).

0955-2219/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2007.07.003

borosilicate glass + alumina system developed by Fujitsu,[18] the lead borosilicate glass + alumina system by DuPont,[19] and the B_2O_3–K_2O–SiO_2–CaO–SrO–BaO glass + alumina system by Motorola.[20,21] However, for the glass–ceramics system, a crystallizable glass was used, e.g., crystallizable cordierite by IBM[22] and crystallizable CaO–B_2O_3–SiO_2 by Ferro.[24] Several these LTCC materials[16,21] such as DuPont 951 ($\varepsilon_r = 7.8$, $\tan\delta = 0.0015$ at 1 kHz), Ferro A6 ($\varepsilon_r = 5.9$, $\tan\delta = 0.002$ at 10 MHz), Heraeus CT 700 ($\varepsilon_r = 7.0$, $\tan\delta = 0.002$ at 1 kHz), Motorola T2000 ($\varepsilon_r = 9.1$, $\tan\delta = 1 \times 10^{-3}$ at 2 GHz), etc., have been used for ceramics packaging and substrate. However, these LTCC materials cannot meet the requirement of microwave dielectric components due to the low $Q \times f$ values.

In this paper, we report a new LTCC microwave dielectric ceramic system CaO–MgO–SiO_2–TiO_2 with the high $Q \times f$ value, low-cost material, and the compatibility of the ceramic sheet with Ag electrodes. Phase constitutes and dielectric properties of $(Ca_{1-x},Mg_x)SiO_3$ ($x = 0.1$–0.5) ceramics were studied with different x contents, and $CaTiO_3$ demonstrated an effective compensation in $(Ca_{1-x},Mg_x)SiO_3$ τ_f value. In addition, we utilized a very small quantity of Li_2CO_3–V_2O_5 combined additives in an attempt to prepare ceramics with even lower sintering temperatures down to 900 °C that could have potential applications as co-fired circuit components. The properties of ceramics slurry, green tape, and the chemical compatibility of silver electrodes, and the LTCC materials have also been investigated.

2. Experimental procedure

Samples of (Ca_{1-x},Mg_x) SiO_3 ($x = 0.1$, 0.2, 0.3, 0.4, 0.5), and $CaTiO_3$ were individually synthesized by conventional solid-state methods from reagent-grade oxide powders (purity higher than 99%): MgO, $CaCO_3$, TiO_2, and SiO_2. The starting materials were mixed according to the desired stoichiometry: $(Ca_{1-x},Mg_x)SiO_3$, and $CaTiO_3$, and ground in ethanol for 16 h in a ball mill with zirconia balls. Both mixtures were dried and calcined at 1100 °C for 4 h in air with subsequent ball milling in ethanol with zirconia balls. After drying and sieving, the calcined $(Ca_{1-x},Mg_x)SiO_3$ powders were uniaxially pressed under a pressure of 100 MPa into disks measuring 18 mm in diameter and 9 mm thickness. The disks covered with crucibles were sintered at 1300 °C for 3 h. The calcined reagents were individually re-milled for 16 h according to the desired composition: $(1-y)CaMgSi_2O_6$–$yCaTiO_3$ and $0.88CaMgSi_2O_6$–$0.12CaTiO_3$ with 0.5–2 wt% Li_2CO_3–V_2O_5. Following the same drying and forming procedures, the $(1-y)CaMgSi_2O_6$–$yCaTiO_3$ and $0.88CaMgSi_2O_6$–$0.12CaTiO_3$ containing Li_2CO_3–V_2O_5 pellets were sintered at 1300 °C for 3 h and 860–960 °C for 2 h, respectively.

The crystalline phases were analyzed by X-ray powder diffraction analysis (XRD) using Cu Kα radiation of 2θ from 10° to 80°. The microstructure observation of the samples was performed by scanning electron microscopy (SEM). The bulk densities of the sintered pellets were measured by the Archimedes method. Microwave dielectric constant ε_r and quality factor values $Q \times f$ at microwave frequencies were measured by the Hakki–Coleman dielectric resonator method[26,27] using an Agilent 8719ET (0.05–13.5 GHz) network analyzer. The temperature coefficient of resonant frequency τ_f was also measured by the same method by changing temperature mainly from −30 to 80 °C and calculated from the equation:

$$\tau_f\,(\mathrm{ppm}/^\circ\mathrm{C}) = \frac{f_{80} - f_{-30}}{f_{25} \times 110} \times 10^6$$

where f_{80}, f_{-30}, and f_{25} are the resonant frequency at 80, −30, and 25 °C, respectively.

3. Results and discussion

Fig. 1 shows the XRD patterns of $(Ca_{1-x},Mg_x)SiO_3$ ceramics with the composition range of $0.1 \le x \le 0.5$. For the example of $x = 0.1$, the XRD profiles of the specimen can be indexed by the $CaSiO_3$ wollastonite structure. Compared with the theoretic XRD patterns of the $CaSiO_3$ wollastonite structure (JCPDS #84-0655), a slight shift in the position of maximum intensity peaks towards the higher side was observed, indicating a decrease in lattice parameter. The result is due to the substitution of Mg^{2+} with the lower ionic radius of 0.78 Å for Ca^{2+} with larger ionic radius of 1.06 Å in the A-site. The $CaMgSi_2O_6$ phase (JCPDS #19-0239) with a C2/c monoclinic structure cell, $a = 9.748$ Å, $b = 8.926$ Å, $c = 5.250$ Å, $\beta = 105.8°$, and $Z = 4$ was observed at $x = 0.2$, which means that the maximum content of Mg solid solution in $CaSiO_3$ is lower than 0.2. The peak intensity of $CaMgSi_2O_6$ increased steadily and that of $CaSiO_3$ decreased with the increase of x in the range of 0.2–0.4. When $x = 0.5$, the phase $CaSiO_3$ disappeared and only the phase $CaMgSi_2O_6$ was observed.

Microwave dielectric properties of $(Ca_{1-x},Mg_x)SiO_3$ ceramics sintered at 1300 °C for 3 h are presented in Table 1. When the x value increased from 0.1 to 0.5, the dielectric constant ε_r increased nonlinearly from 6.49 to 7.46, the $Q \times f$ values firstly decreased from 62,420 to 48,784 GHz and then increased to 59,638 GHz, and no remarkable variations in the τ_f were

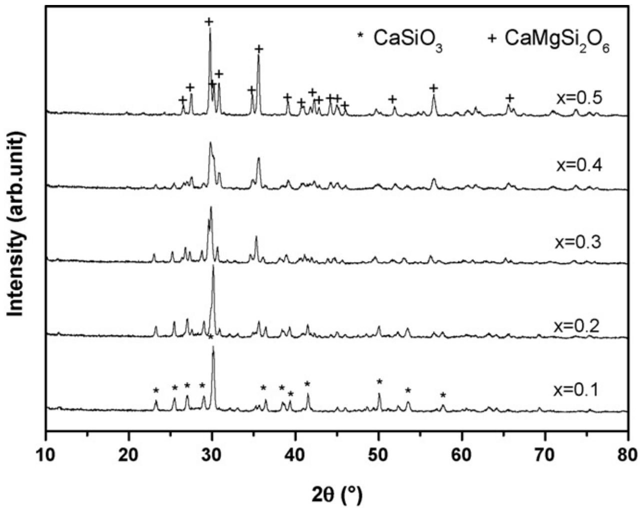

Fig. 1. XRD patterns of $(Ca_{1-x},Mg_x)SiO_3$ ceramics ($0.1 \le x \le 0.5$) sintered at 1300 °C for 3 h.

Table 1
Microwave dielectric properties of $(Ca_{1-x},Mg_x)SiO_3$ ceramics sintered at 1300 °C for 3 h

x value	ε_r	$Q \times f$ (at 8 GHz)	τ_f (ppm/°C)
0.1	6.49	62,300	−43.8
0.2	6.52	53,700	−43.2
0.3	6.79	48,800	−46.4
0.4	7.35	53,800	−45.7
0.5	7.46	59,700	−42.3

Table 2
Microwave dielectric properties of $(1-y)CaMgSi_2O_6 + yCaTiO_3$ ceramics sintered at 1300 °C for 3 h

y value	ε_r	$Q \times f$ (at 8 GHz)	τ_f (ppm/°C)
0.05	8.25	56,200	−27.5
0.08	8.78	54,100	−14.7
0.10	9.09	52,300	−6.9
0.12	9.42	50,800	+5.6
0.15	9.81	47,500	+13.7

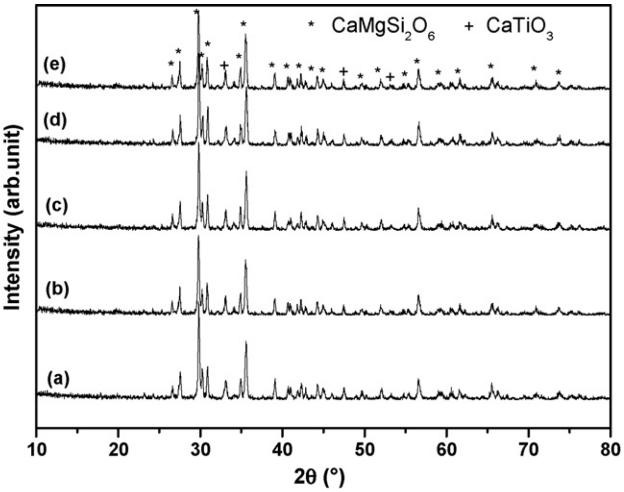

Fig. 2. XRD patterns of ceramics with (a) 0.5 wt%, (b) 1 wt%, (c) 1.5 wt%, and (d) 2 wt% Li_2CO_3–V_2O_5 addition sintered at 880 °C for 2 h, and (e) no addition sintered at 1300 °C for 3 h.

observed. As shown in the XRD patterns (Fig. 1), single-phased $CaSiO_3$, and $CaMgSi_2O_6$ were observed at composition $x = 0.1$ and 0.5, respectively. It indicated that the ε_r of $CaSiO_3$ and $CaMgSi_2O_6$ were 6.49 and 7.46, respectively. Thus, it could conclude that the ionic polarizability of $CaMgSi_2O_6$ is higher than that of $CaSiO_3$. In general, because a near-zero τ_f value of dielectric ceramics is necessary for commercial applications, an improvement in τ_f value, closer to 0 ppm/°C, is required in this system.

In order to acquire the closer zero τ_f, $CaTiO_3$ was added to $CaMgSi_2O_6$. Table 2 demonstrates the microwave dielectric properties of $(1-y)CaMgSi_2O_6$–$yCaTiO_3$ ceramic system sintered at 1300 °C for 3 h. As x value increased from 0.05 to 0.15, the τ_f values of $(1-y)CaMgSi_2O_6$–$yCaTiO_3$ ceramics varied from −27.5 to 13.7 ppm/°C. Since the τ_f went through zero, it indicates that zero τ_f value can be obtained by appropriately adjusting the y value of $(1-y)CaMgSi_2O_6$–$yCaTiO_3$ ceramics. The XRD patterns of $0.88CaMgSi_2O_6$–$0.12CaTiO_3$ sintered at 1300 °C for 3 h is shown in Fig. 2(e). The XRD patterns showed that peaks indicating the presence $CaMgSi_2O_6$ as the main crystalline phase, in association with $CaTiO_3$ phase. It also indicated that solid solution did not form in $CaMgSi_2O_6$–$CaTiO_3$ ceramic system due to the structure difference of $CaMgSi_2O_6$ (monoclinic structure) and $CaTiO_3$ (orthorhombic structure).

To further decrease the sintering temperature of this new microwave dielectric ceramic $0.88CaMgSi_2O_6$–$0.12CaTiO_3$, small contents of Li_2CO_3–V_2O_5 were doped into the samples. Fig. 2(a)–(d) presents the XRD patterns of the ceramics sintered at 880 °C for 2 h with different amounts of Li_2CO_3–V_2O_5. It could be observed that all the compounds exhibit the mixture of $CaMgSi_2O_6$ phase and $CaTiO_3$ phase, similar to those shown in Fig. 2(e). The SEM images of $0.88CaMgSiO_6$–$0.12CaTiO_3$ ceramics with 1 and 1.5 wt% Li_2CO_3–V_2O_5 sintered at 880 °C are shown in Fig. 3. Probably because of the liquid phase, the denser microstructures and almost no pores were found.

Fig. 4 shows the densities and microwave dielectric properties of the $0.88CaMgSi_2O_6$–$0.12CaTiO_3$ ceramics with Li_2CO_3–V_2O_5 sintered at optimal temperatures. The optimum temperature for samples with 0.5 and 1–2 wt% additive were 930 and 880 °C. From Fig. 4, it can be seen that the densities of sam-

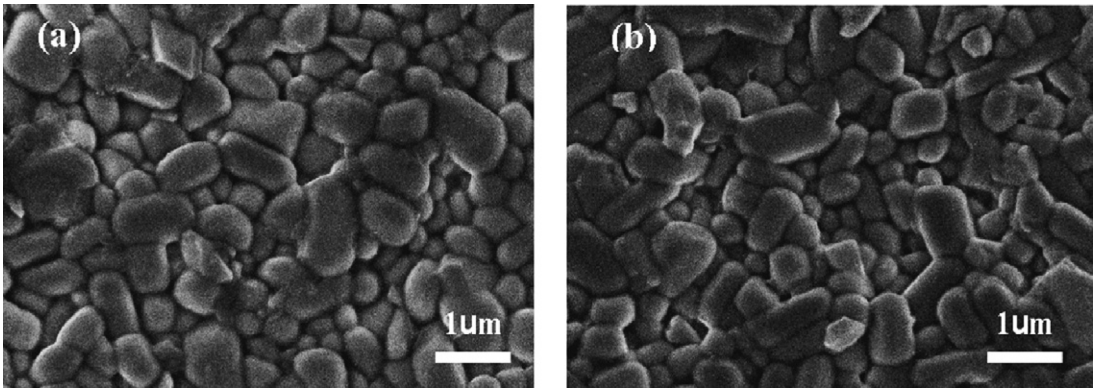

Fig. 3. SEM micrographs of the polished surface of the ceramics with (a) 1 wt% Li_2CO_3–V_2O_5 and (b) 1.5 wt% Li_2CO_3–V_2O_5 sintered at 880 °C for 2 h.

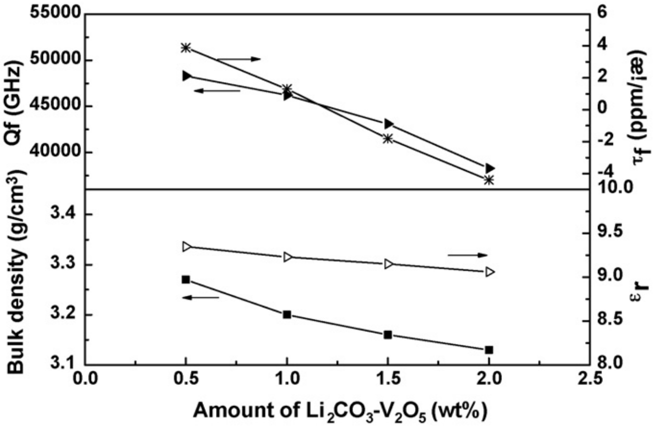

Fig. 4. Densities and microwave dielectric properties of $0.88CaMgSi_2O_6$–$0.12CaTiO_3$ ceramics with Li_2CO_3–V_2O_5 content of 0.5 and 1–2 wt%, sintered for 2 h at 930 and 880 °C, respectively.

ples with 0.5–2 wt% were more than $3.12\,g/cm^3$, which means that the Li_2CO_3–V_2O_5 is a very effective low-temperature additive. The density decreased slowly as the Li_2CO_3–V_2O_5 content increased. The dielectric constant ε_r changed in manner similar to density, which decreased slightly from about 9.35 to 9.06 as the Li_2CO_3–V_2O_5 content increased from 0.5 to 2 wt%. The decrease in $Q \times f$ value was probably due to the existence of unknown second phase with the increase of Li_2CO_3–V_2O_5. As increasing Li_2CO_3–V_2O_5 content, τ_f tends to be shifted to negative region linearly and varied from 3.9 ppm/°C at 0.5 wt% Li_2CO_3–V_2O_5 addition to −4.4 ppm/°C at 2 wt% Li_2CO_3–V_2O_5 addition. This implies that the τ_f values of the ceramics could be adjusted to near zero by adding slightly more Li_2CO_3–V_2O_5. Thus, it is obvious that these ceramics might be good candidates for LTCCs, and for 1 wt% Li_2CO_3–V_2O_5, ceramics with density $\rho = 3.22\,g/cm^3$, $\varepsilon_r = 9.23$, $Q \times f = 46{,}200$ GHz, and $\tau_f = 1.3$ ppm/°C could be obtained at $T_s = 880$ °C.

In order to investigate ceramics slurry for tape casting, the powders were first mixed with solvents and dispersant in a ball mill for 24 h, and then plasticizers and binder were added, and mixed for another 24 h to obtain the slurry. The solvents were toluol and ethanol. The dispersant was menhaden fish oil (OA85). The binder itself was polyvinyl butyral (BM-2), and the compatible plasticizer was butyl benzyl phthalate (S160). The tape casting was done with caster (TM-MC-500). The ceramics slurry viscosity was 1200 mPa S. Generally, ceramics slurries with viscosity of 500–2500 mPa S are suitable for the tape casting process.[28] Fig. 5 shows the microstructures of green tapes. In the green state, the average particle sizes of LTCC ceramics was around 1 μm, and the microstructures of green tapes were uniform and there was no existence of agglomerates. On the other hand, the surface of green tape was glabrous; the green tape had very high density and tensile strength.

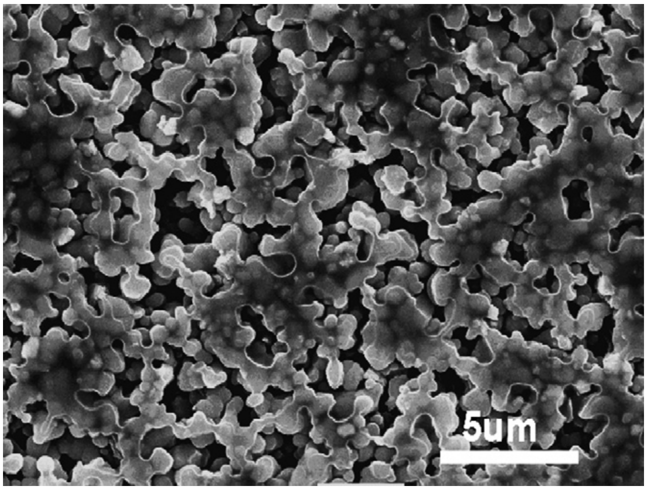

Fig. 5. SEM micrograph of the green tape.

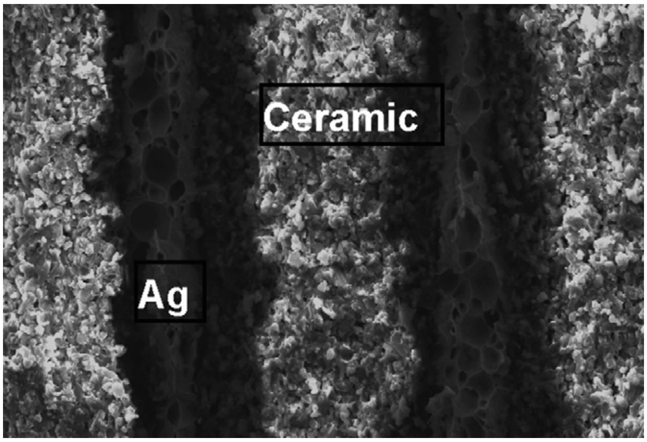

Fig. 6. SEM micrograph of $0.88CaMgSi_2O_6$–$0.12CaTiO_3$ ceramics with 1 wt%. Li_2CO_3–V_2O_5 samples co-fired with Ag in air at 880 °C for 2 h.

For compatibility tests, ceramics sheet with Ag electrodes were co-fired and analyzed to detect interactions between the low-fired samples and electrodes. SEM analysis revealed no interaction forming new phases after firing, as shown in Fig. 6. It is obvious that reaction of LTCC materials with Ag electrodes did not occur. Therefore, $CaMgSi_2O_6$–$CaTiO_3$ with Li_2CO_3–V_2O_5 could be selected as suitable candidates for LTCC materials, because of low sintering temperature, good microwave dielectric properties, and compatibility with electrodes.

4. Conclusions

In this study, phase constitutes and dielectric properties of $(Ca_{1-x},Mg_x)SiO_3$ ($x = 0.1$–0.5) ceramics were studied with different x contents, and $CaTiO_3$ demonstrated an effective compensation in $(Ca_{1-x},Mg_x)SiO$ τ_f value. The $0.88CaMgSi_2O_6$–$0.12CaTiO_3$ composition was selected, due to its reasonable dielectric properties: $\varepsilon_r = 9.42$, $Q \times f = 50{,}800$ GHz, and $\tau_f = 5.6$ ppm/°C. The addition of ≤2.0 wt% Li_2CO_3–V_2O_5 was very effective in lowering the sintering temperature (T_s), and dense ceramics could be obtained at $T_s \leq 900$ °C. The addition of Li_2CO_3–V_2O_5 does not induce apparent degradation in the microwave properties. It was found that dielectric constant (ε_r) and the quality factor ($Q \times f$) decreased, the temperature coefficient of resonant frequency (τ_f) shifted to a negative value with the increase amount of Li_2CO_3–V_2O_5 addition. The specimens with 1 wt% Li_2CO_3–V_2O_5 sintered at 880 °C for 2 h shows excellent dielectric properties: $\varepsilon_r = 9.23$, $Q \times f = 46{,}200$ GHz, and $\tau_f = 1.3$ ppm/°C. The low-temperature sintering ceramics powders were suitable for the tape casting process. Also, the material is compatible with Ag electrodes and, therefore, is suitable for LTCC application.

References

1. Ding, S. H., Yao, X., Mao, Y. and Liu, P. L., Microwave dielectric properties of $(Bi_{1-x}R_x)NbO_4$ ceramics (R = Ce, Nd, Dy, Er). *J. Eur. Ceram. Soc.*, 2006, **26**, 2003–2005.
2. Shin, H. K., Shin, H., Cho, S. Y. and Hong, K. S., Phase evolution and dielectric properties of $MgTiO_3$–$CaTiO_3$-based ceramic sintered with lithium borosilicate glass for application to low-temperature co-fired ceramics. *J. Am. Ceram. Soc.*, 2005, **88**, 2461–2465.
3. Kim, H. T., Kim, S. H., Nahm, S., Byun, J. D. and Kim, Y., Low-temperature sintering and microwave dielectric properties of zinc metatitanate–rutile mixtures using boron. *J. Am. Ceram. Soc.*, 1999, **82**, 3043–3048.
4. Zhang, Q. L., Yang, H., Zou, J. L. and Wang, H. P., Sintering and microwave dielectric properties of LTCC–zinc titanate multilayers. *Mater. Lett.*, 2005, **59**, 880–884.
5. Huang, W., Liu, K. S., Chu, L. W., Hsiue, G. H. and Lin, I. N., Microwave dielectric properties of LTCC materials consisting of glass–$Ba_2Ti_9O_{20}$ composites. *J. Eur. Ceram. Soc.*, 2003, **23**, 2559–2563.
6. Zhang, Y. C., Li, L. T., Yue, Z. X. and Gui, Z. L., Effects of additives on microstructures and microwave dielectric properties of $ZnNb_2O_6$ ceramics. *Mater. Sci. Eng. B*, 2003, **99**, 282–285.
7. Tong, J. X., Zhang, Q. L., Yang, H. and Zou, J. L., Low-temperature firing and microwave dielectric properties of $Ca[(Li_{1/3}Nb_{2/3})_{0.84}Ti_{0.16}]O_{3-\delta}$ ceramics for LTCC applications. *J. Am. Ceram. Soc.*, 2007, **90**, 845–849.
8. Lim, J. B., Cho, K. H., Nam, S., Paik, J. H. and Kim, J. H., Effect of $BaCu(B_2O_5)$ on the sintering and microwave dielectric properties of BaO–Ln_2O_3–TiO_2 (Ln = Sm, Nd) cermics. *Mater. Res. Bull.*, 2006, **41**, 1868–1874.
9. Cho, I. S., Kim, D. W., Kim, J. R. and Hong, K. S., Low-temperature sintering and microwave dielectric properties of $BaO\cdot(Nd_{1-x}Bi_x)_2O_3\cdot4TiO_2$ by the glass additions. *Ceram. Int.*, 2004, **30**, 1181–1185.
10. Borisevich, A. Y. and Davies, P. K., Effect of doping on the sintering and dielectric properties of M-phase $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ ceramics. *J. Am. Ceram. Soc.*, 2004, **87**, 1047–1052.
11. Kim, M. H., Jeong, Y. H., Nahm, S., Kim, H. T. and Lee, H. J., Effect of B_2O_3 and CuO additives on the sintering temperature and microwave dielectric properties of $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramics. *J. Eur. Ceram. Soc.*, 2006, **26**, 2139–2142.
12. Kim, D. W., Hong, K. S., Yoon, C. S. and Kim, C. K., Low-temperature sintering and microwave dielectric properties of $Ba_5Nb_4O_{15}$–$BaNb_2O_6$ mixtures for LTCC applications. *J. Eur. Ceram. Soc.*, 2003, **23**, 2597–2601.
13. Umemura, R., Ogawa, H., Ohsato, H., Kan, A. and Yokoi, A., Microwave dielectric properties of low-temperature sintered $Mg_3(VO_4)_2$ ceramic. *J. Eur. Ceram. Soc.*, 2005, **25**, 2865–2870.
14. Umemura, R., Ogawa, H., Ohsato, H. and Kan, A., Low-temperature sintering microwave dielectric properties relations in $Ba_3(VO_4)_2$ ceramic. *J. Alloy. Compd.*, 2006, **424**, 388–393.
15. Bian, J. J., Kim, D. W. and Hong, K. S., Glass-free LTCC microwave dielectric ceramics. *Mater. Res. Bull.*, 2005, **40**, 2120–2129.
16. Jantunen, H., Rautioaho, R., Uusimäki, A. and Leppävuori, S., Compositions of $MgTiO_3$–$CaTiO_3$ ceramic with two borosilicate glasses for LTCC technology. *J. Eur. Ceram. Soc.*, 2000, **20**, 2331–2336.
17. Kim, E. S., Kim, S. H. and Lee, B. I., Low-temperature sintering and microwave dielectric properties of $CaWO_4$ ceramics for LTCC applications. *J. Eur. Ceram. Soc.*, 2006, **26**, 2101–2104.
18. Imanka, Y. and Kamehara, N., Influence of shrinkage mismatch between copper and ceramics on dimensional control of the multilayer ceramic circuit board. *J. Ceram. Soc. Jpn. Int. Ed.*, 1992, **100**, 558–561.
19. Steinberg, J. I., Horowitz, S. J. and Bacher, R. J., Low-temperature co-fired tape dielectric material systems for multilayer interconnections, advances in ceramics. In *Multilayer Ceramic Devices*, *19*, ed. J. B. Blum and W. R. Canon. American Ceramic Society, Westerville, OH, 1986, pp. 31–39.
20. Jean, J. J. and Fang, Y. C., Devitrification kinetics and mechanism of K_2O–CaO–SrO–BaO B_2O_3–SiO_2 glass–ceramic. *J. Am. Ceram. Soc.*, 2001, **84**, 1354–1360.
21. Dai, S. X., Huang, R. F. and Wilcox, D. L., Use of titanates to achieve a temperature-stable low-temperature co-fired ceramic dielectric for wireless applications. *J. Am. Ceram. Soc.*, 2002, **85**, 828–832.
22. Tummala, R. R., Ceramic and glass–ceramic packaging in the 1990s. *J. Am. Ceram. Soc.*, 1991, **74**, 895–908.
23. Knickerbocker, S. H., Kumar, A. H. and Herron, L. W., Cordierite glass–ceramics for ceramic packaging. *Am. Ceram. Soc. Bull.*, 1993, **72**(1), 90–95.
24. Chang, C. R. and Jean, J. J., Crystallization kinetics and mechanism of low-dielectric, low-temperature, cofirable CaO–B_2O_3–SiO_2 glass–ceramics. *J. Am. Ceram. Soc.*, 1999, **82**, 1725–1732.
25. Zhu, H. K., Liu, M., Zhou, H. Q., Li, L. Q. and Lv, A. G., Study on properties of CaO–B_2O_3–SiO_2 system glass–ceramic. *Mater. Res. Bull.*, 2007, **42**, 1137–1144.
26. Hakki, B. W. and Coleman, P. D., A dielectric resonator method of measuring inductive capacitors in the millimeter range. *IEEE Trans. Microwave Theor. Technol.*, 1960, **8**, 402–410.
27. Courtey, W. E., Analysis and evaluation of a method of measuring the complex permittivity and permeability microwave insulators. *IEEE Trans. Microwave Theor. Technol.*, 1970, **18**, 475–485.
28. Brook, R. J., Materials Science and Technology. In *Processing of Ceramics Part I, vol. 17A*. Science Press, Beijing, 1999, p. 206, Translated by State Key Laboratory of New Ceramic and Fine Processing of Tsinghua University.