

Effect of the B_2O_3 addition on the sintering behavior and microwave dielectric properties of $Ba_3(VO_4)_2-Zn_{1.87}SiO_{3.87}$ composite ceramics

Yang Lv, Ruzhong Zuo*

Institute of Electro Ceramics & Devices, School of Materials Science and Engineering, Hefei University of Technology, Tunxi Road 193, Hefei 230009, PR China

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Abstract

The effect of the B_2O_3 addition on the low-temperature sintering, microstructure and microwave dielectric properties of the $Ba_3(VO_4)_2-Zn_{1.87}SiO_{3.87}$ composite ceramics was investigated. The results indicate that the addition of B_2O_3 can effectively promote the densification and further improve the microwave dielectric properties of the composite. The low-temperature sintering mechanism was ascribed to the formation of the liquid phase owing to the reaction between the additive B_2O_3 and the residual SiO_2 in the composite. $B_2O_3-SiO_2$ liquid phases can not only lower the sintering temperature, but also speed up the grain growth of the composite ceramics. The rapid grain growth occurs as the B_2O_3 content is more than 6 wt. The 3 wt B_2O_3 doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ ceramics can be well sintered at 925 °C and exhibit excellent microwave dielectric properties of $Q \times f \sim 40,800$ GHz, $\epsilon_r \sim 10$ and $\tau_f \sim 0.5$ ppm/°C. © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: A. Sintering; B. Composite; LTCC; Microwave dielectric properties

1. Introduction

For satisfying the requirement of multilayer substrates at microwave frequencies, the dielectric materials should not only have a high quality factor ($Q \times f$), a low dielectric constant (ϵ_r), and a zero-near temperature coefficient of the resonant frequency (τ_f), but also own lower sintering temperatures than the melting point of the electrode metals (for example, 961 °C for silver or 1064 °C for copper) [1–6]. Particularly, the low-temperature sintering is a critical requirement for commercial low-temperature confirmable ceramic (LTCC) technology.

The composite processing enables tunable microwave dielectric properties. That is to say, zero-near τ_f values can be realized and simultaneously desirable microwave dielectric properties (ϵ_r and $Q \times f$) can be maintained. Our previous studies indicated that $Ba_3(VO_4)_2-Zn_{1.87}SiO_{3.87}$ composite ceramics could satisfy the above requirements, as the weight ratio of two phases was appropriately adjusted. The $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ (weight fraction) composite

ceramics sintered at 1100 °C can achieve a low dielectric constant ($\epsilon_r = 9.3$) and a near-zero τ_f value (-8.3 ppm/°C) [7]. However, their relatively high sintering temperature needs to be decreased in order to cofire with the silver paste. It was reported that the residual SiO_2 might exist in the calcined $Zn_{1.87}SiO_{3.87}$ powders due to the deficiency of ZnO compared to the stoichiometric Zn_2SiO_4 ceramic. As a result, the $Q \times f$ values of the composites were greatly deteriorated ($Q \times f = 24800$ GHz), compared to those of pure-phase those of pure-phase $Ba_3(VO_4)_2$ ($Q \times f = 50000$ GHz) or $Zn_{1.87}SiO_{3.87}$ ($Q \times f = 147000$ GHz) [8,9].

In order to decrease the sintering temperature of the ceramics, low-melting-point compounds such as B_2O_3 , Li_2CO_3 , V_2O_5 and $BaCu(B_2O_5)$ were used as conventional additives [10–17]. According to the phase diagram of $B_2O_3-SiO_2$ binary system [18], there is a wide borosilicate liquid phase region. With increasing the content of B_2O_3 , the temperature for the liquid phase rapidly decreases. Considering that the B_2O_3 additive could react with the residual SiO_2 in the non-stoichiometric $Zn_{1.87}SiO_{3.87}$, an appropriate amount of B_2O_3 was used to improve the densification behavior of the $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ composite ceramic in this study. Moreover, the effect of the B_2O_3

*Corresponding author. Tel.: +86 551 2905285; fax: +0086 551 2905285.

E-mail address: piezolab@hfut.edu.cn (R. Zuo).

addition on the microstructure and microwave dielectric properties was investigated as well.

2. Experimental procedure

The x wt B_2O_3 ($1 \leq x \leq 6$) doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ ceramics were synthesized via a conventional solid-state reaction method using high-purity chemical reagents (>99). $Ba_3(VO_4)_2$ was obtained by calcining the mixture of $BaCO_3$ and V_2O_5 in a molar ratio of 3:1 at $800^\circ C$ for 4 h. The non-stoichiometric $Zn_{1.87}SiO_{3.87}$ powder was prepared by calcining the powder mixture of ZnO and SiO_2 at $1150^\circ C-1175^\circ C$ for 2 h. Subsequently, the calcined powders were mixed with different amounts of H_3BO_3 . After that, the above mixture was then re-milled for 4 h together with 5 wt PVA solution using zirconium balls and alcohol as the milling medium. The slurries were dried, and then pressed into cylinders with dimensions of 10 mm in diameter and 7–8 mm in height. These specimens were first heated at $550^\circ C$ in air for 4 h to burn out the organic binder, and then sintered in air in the temperature range of $900^\circ C-1000^\circ C$ for 4 h.

The bulk density of the sintered samples was measured by the Archimedes method. The relative density of the specimens was obtained according to the bulk density and the theoretical densities. The theoretical density of the composite ceramic was calculated using the following equation [19]:

$$\rho = \frac{w_1 + w_2}{w_1/\rho_1 + w_2/\rho_2} \quad (1)$$

Where ρ_1 and ρ_2 are the theoretical densities of $Ba_3(VO_4)_2$ and $Zn_{1.87}SiO_{3.87}$, respectively [8,9], and w_1 and w_2 are the mass fractions of $Ba_3(VO_4)_2$ and $Zn_{1.87}SiO_{3.87}$, respectively. The crystal structure of the calcined powders and sintered ceramics was examined by an X-ray diffractometer (XRD, D/Max2500V, Rigaku, Japan) using CuK radiation. The grain morphology was analyzed by a scanning electron microscope (SEM, SSX-550, Shimadzu, Japan). An N5230C network analyzer (Agilent, Santa Clara, CA, USA) was used for the measurement of microwave dielectric properties by means of a Hakki–Coleman method [20]. The τ_f value of the samples was measured in the temperature range from $30^\circ C$ to $80^\circ C$. It can be calculated by the following relationship: $f = f_1 - f_2 / f_1(T_1 - T_2)$ where f_1 and f_2 represent the resonant frequencies at T_1 and T_2 , respectively.

3. Results and discussion

Fig. 1 shows the XRD patterns of the x wt ($0 \leq x \leq 6$) B_2O_3 -doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ composite ceramics sintered at $950^\circ C$ for 4 h. The main diffraction peaks could be assigned to the $Ba_3(VO_4)_2$ (JCPDS#29-0211) and $Zn_{1.87}SiO_{3.87}$ (JCPDS#37-1485) phases, in addition to some minor peaks for unknown phases. This result indicates that the composite ceramic has been basically formed.

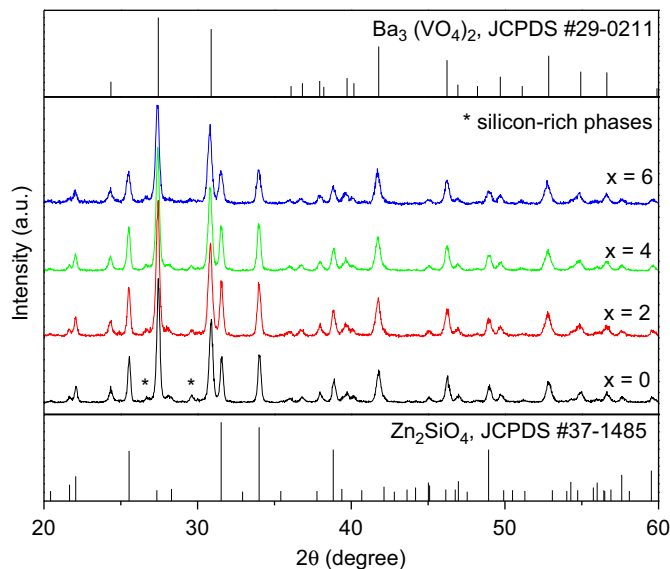


Fig. 1. XRD patterns of the x wt B_2O_3 -doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ composite ceramics sintered at $950^\circ C$ for 4 h.

$Ba_3(VO_4)_2$ is a hexagonal structure (R32/m) in which V^{5+} ions are located in the center of tetrahedral $[VO_4]$ units linked by sixfold and tenfold coordinate Ba^{2+} ions [21]. However, $Zn_{1.87}SiO_{3.87}$ has a rhombohedral symmetry and Zn^{2+} occupies the tetrahedral site of $[ZnO_4]$ units [22]. On the basis of our previous studies [7], the amount of unknown phases was reduced with decreasing the $Zn_{1.87}SiO_{3.87}$ content in the composite, which suggests that they are probably silicon-rich phases. It can be observed that the diffraction peak intensity of the unknown phases was slightly reduced as B_2O_3 was added, probably because a part of the secondary phases changed into borosilicate-based glass phases after sintering.

The relative density of the x wt B_2O_3 -doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ composite ceramic as a function of the sintering temperature is shown in Fig. 2. On the one hand, the relative density of all specimens increases with the addition of B_2O_3 , and then starts to decline after a maximum value. On the other hand, the sample densities also first increase with increasing the sintering temperature and then start to decrease as the temperature is too high. The possible reason might be ascribed to the reduced sintering driving force owing to the grain coarsening induced by a liquid phase at higher temperatures. For the specimens doped with <3 wt B_2O_3 , a maximum relative density up to 97 can be obtained as the sample is sintered at $\sim 950^\circ C$. As the B_2O_3 content is 4 wt or 5 wt, specimens reach the highest relative density at $925^\circ C$. Moreover, as the doping content of B_2O_3 is 6 wt, the optimum sintering temperature of the specimen can be further decreased to $900^\circ C$. The liquid phase line of the B_2O_3 and SiO_2 in the phase diagram (see inset of Fig. 2) indicates that the temperature for the solid–liquid phase line decreases from $920^\circ C$ at 46 mol B_2O_3 , $870^\circ C$ at 50 mol B_2O_3 , to $830^\circ C$ at 55 mol B_2O_3 [18]. For the B_2O_3 doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ composite

ceramics, the molar fraction of B_2O_3 and SiO_2 could be obtained from the weight fractions of B_2O_3 and $Zn_{1.87}SiO_{3.87}$, as shown in Table 1. The molar amount of residual SiO_2 in the $Zn_{1.87}SiO_{3.87}$ ceramic can be calculated by using the following equation: $Zn_{1.87}SiO_{3.87} \rightarrow 0.935 Zn_2SiO_4 + 0.065 SiO_2$. It can be seen that the optimum sintering temperature of the x wt B_2O_3 doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ composite ceramic is actually higher than the corresponding melting point of the $B_2O_3-SiO_2$ binary system (the liquid line of the phase diagram). This result means that the densification behavior of $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ ceramics can be not only affected by the temperature at which the liquid starts to appear, but also by the amount of the liquid phase.

The SEM micrographs of the B_2O_3 -doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ ceramics are shown in Fig. 3. Fig. 3(a–d) show the grain morphology of the specimens doped with different B_2O_3 contents and sintered at $950^\circ C$. For the B_2O_3 -free specimens (Fig. 3 (a)), many pores still remain in the sintered sample owing to an insufficient densification. The specimens are found to be denser with increasing the B_2O_3 content. Simultaneously, the grain size becomes larger as well. It is indicated that $B_2O_3-SiO_2$ liquid phase can not only improve the densification behavior by speeding up the particle rearrangement at the early period of sintering and mass transportation at the middle period of sintering, but also can slightly promote

the grain growth [23]. As the B_2O_3 content is 6 wt, the excess amount of the low-melting-point liquid phases tends to induce rapid grain growth in the sintered body, as shown in Fig. 3 (e). Nevertheless, all specimens exhibit a composite structure of bimodal grain size distribution. Fig. 3 (f, c and g) show the grain morphology of the 3 wt B_2O_3 doped specimens sintered at $900^\circ C$, $950^\circ C$ and $1000^\circ C$, respectively. It can be observed that the grain size of the composite ceramic increases obviously with the sintering temperature, such that the sample densities start to decrease at higher sintering temperatures.

Fig. 4 shows the dielectric constant ϵ_r of the B_2O_3 doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ composite ceramics sintered at different temperatures. With increasing the sintering temperature from $900^\circ C$ to $1000^\circ C$, the ϵ_r values of the specimens slightly change from 7.8 to 10.2. It can be also seen that the ϵ_r values are highly dependent on the relative density of the sintered bodies. Therefore, the tendency of the dielectric constant with the sintering temperature and the B_2O_3 content (Fig. 4) is very similar to that of the relative density (Fig. 2). Glass phases or porosity with low ϵ_r tends to degrade the dielectric property based on the mixing rule of dielectrics as expressed by the Maxwell–Wagner's equation, although decreased grain boundary volume might slightly enhance it owing to an increase in grain size. The 3 wt B_2O_3 doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ composite ceramics have a dielectric constant of ~ 10 as sintered at $925^\circ C$.

Fig. 5 shows the $Q \times f$ value of the B_2O_3 doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ composite ceramics sintered at various temperatures. It can be seen that the $Q \times f$ values of the specimens doped with a small amount of B_2O_3 are very low due to their low relative density. However, the $Q \times f$ values were considerably increased to a maximum value of 40,800 GHz for the 3 wt B_2O_3 doped specimen sintered at $925^\circ C$. The $Q \times f$ value starts to decrease as more amount of B_2O_3 was added, probably due to the reduced density and the increased amount of borosilicate glass phases. The reduced density leads to an increase of the extrinsic losses. The undoped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ composite ceramics sintered at $1100^\circ C$ exhibit a low $Q \times f$ value of 24,800 GHz. The reason could be attributed to the existence of the silicon-rich secondary phases and the ion inter-diffusion between the $Ba_3(VO_4)_2$ and $Zn_{1.87}SiO_{3.87}$ [7]. However, the 3 wt B_2O_3 doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ composite ceramics sintered only at $925^\circ C$ can achieve a modified $Q \times f$ value of 40,800 GHz. This result indicates that B_2O_3

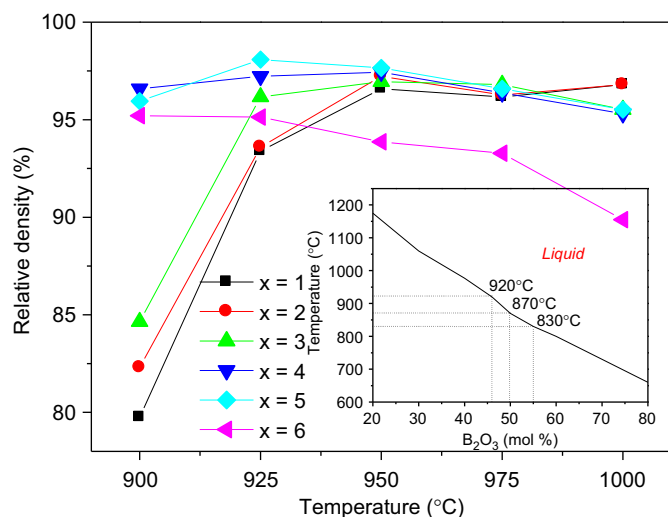


Fig. 2. The variation in the relative density of the x wt B_2O_3 -doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ composite ceramics as a function of the sintering temperature. The inset is the solid-liquid phase line in $B_2O_3-SiO_2$ phase diagram.

Table 1

The optimum sintering temperature of the x wt B_2O_3 doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ ceramics and the corresponding melting points in the $B_2O_3-SiO_2$ phase diagram.

B_2O_3 content (wt)	1	2	3	4	5	6
Optimum sintering temperature ($^\circ C$)	1000	975	950	925	925	900
B_2O_3/SiO_2 molar ratio ()	48	65	74	79	83	85
Temperatures at liquid lines ($^\circ C$)	890	760	700	660	620	600

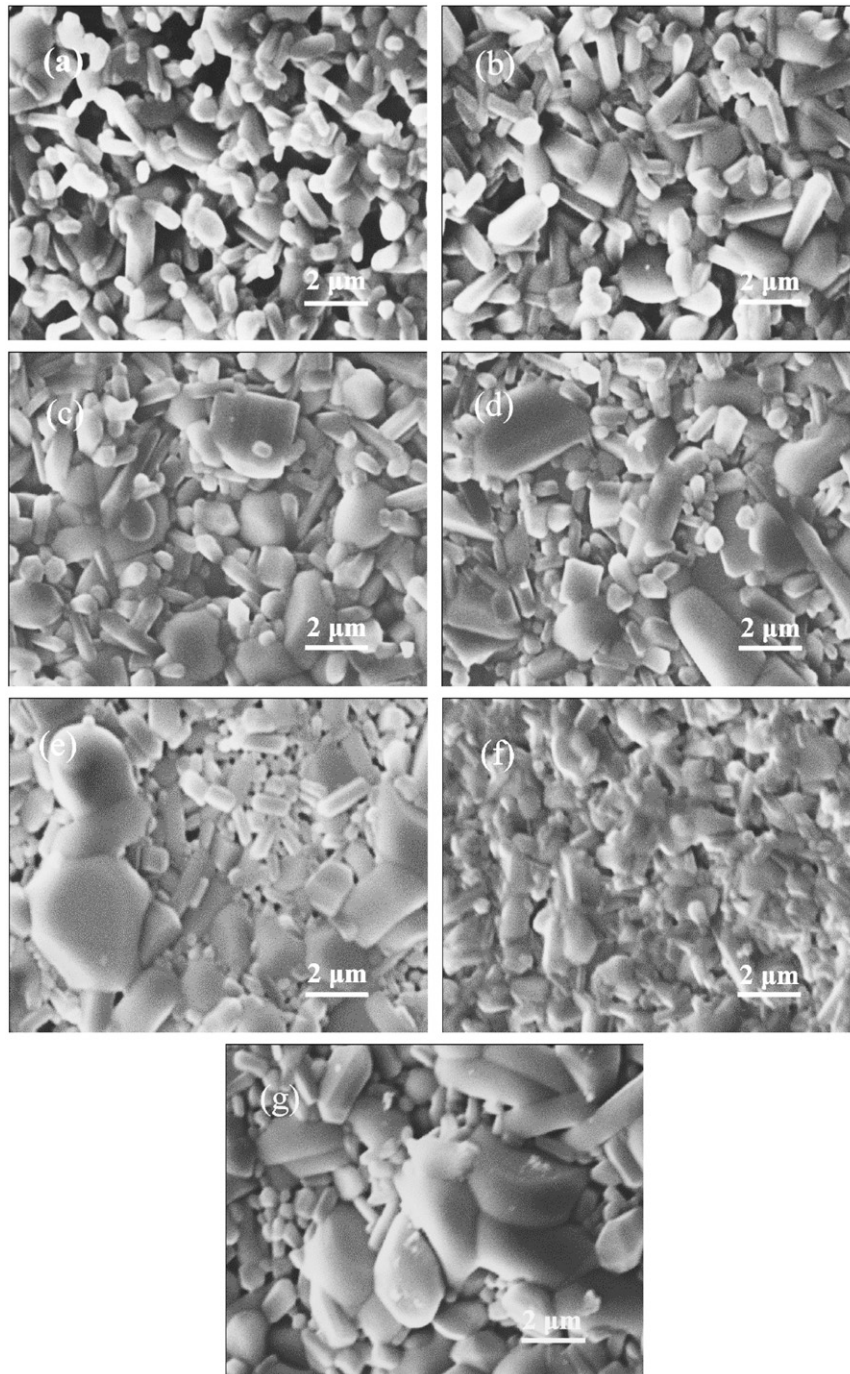


Fig. 3. SEM images of the x wt B_2O_3 -doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ composite ceramics sintered: (a) $x=0$, at $950\text{ }^{\circ}C$, (b) $x=1$, at $950\text{ }^{\circ}C$, (c) $x=3$, at $950\text{ }^{\circ}C$, (d) $x=5$, at $950\text{ }^{\circ}C$, (e) $x=6$, at $900\text{ }^{\circ}C$, (f) $x=3$, at $900\text{ }^{\circ}C$ and (g) $x=3$, at $1000\text{ }^{\circ}C$.

is an effective additive for both the densification and the microwave dielectric properties.

The τ_f value of the B_2O_3 doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ composite ceramics sintered at $925\text{ }^{\circ}C$ is indicated in Fig. 6. It can be seen that the variation in τ_f value with respect to the B_2O_3 content is not significant and ranges from $-8.3\text{ ppm}/^{\circ}C$ to $2.6\text{ ppm}/^{\circ}C$. The 3 wt B_2O_3 -doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ composite ceramics sintered at $925\text{ }^{\circ}C$ exhibit good microwave

dielectric properties of $\epsilon_r \sim 10$, $Q \times f \sim 40800\text{ GHz}$ and $\tau_f \sim 0.5\text{ ppm}/^{\circ}C$. In addition, the 5 wt B_2O_3 -doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ composite ceramics sintered at $900\text{ }^{\circ}C$ also have promising microwave dielectric properties of $\epsilon_r = 9.8$, $Q \times f = 34300\text{ GHz}$, and $\tau_f = 1.1\text{ ppm}/^{\circ}C$. Therefore, it can be believed that the B_2O_3 -doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ composite ceramic could be a good candidate material for low-permittivity microwave LTCC applications.

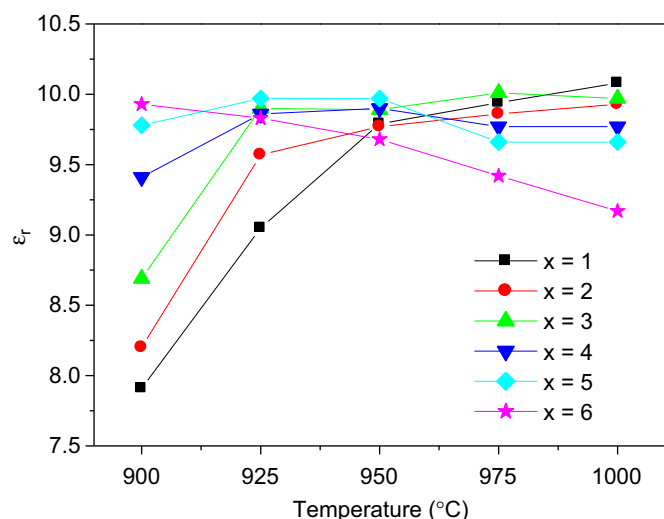


Fig. 4. Dielectric constant of the x wt B_2O_3 -doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ composite ceramics as a function of the sintering temperature.

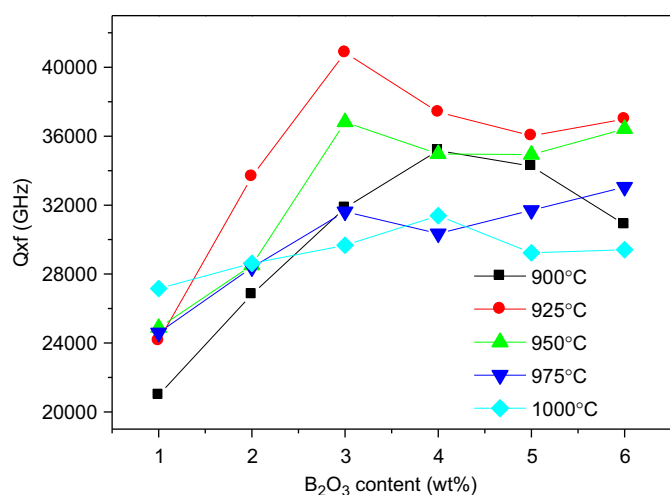


Fig. 5. The $Q \times f$ values of the x wt B_2O_3 -doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ composite ceramics sintered at various temperatures.

4. Summary

The low-temperature sintering behavior, microstructure and microwave dielectric properties of the B_2O_3 doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ composite ceramics were investigated in this study. The results indicate that the low-temperature sintering mechanism was ascribed to the formation of a low-melting-point liquid phase between the B_2O_3 additive and the residual SiO_2 in the composite. An appropriate amount of B_2O_3 can not only promote the densification of the composite ceramics, but also can improve the microwave dielectric properties. The 3 wt B_2O_3 doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ composite ceramics sintered at $925^\circ C$ can exhibit excellent microwave dielectric properties of $\epsilon_r \sim 10$, $Q \times f \sim 40,800$ GHz, and $\tau_f \sim 0.5$ pm/ $^\circ C$.

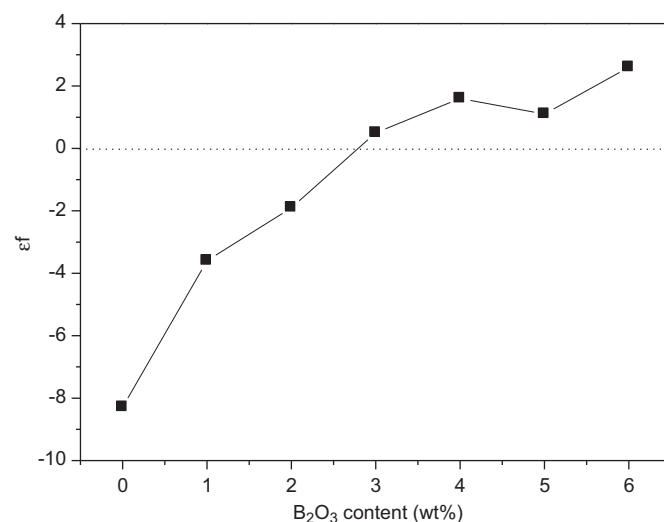


Fig. 6. The τ_f values of the x wt B_2O_3 doped $0.5Ba_3(VO_4)_2-0.5Zn_{1.87}SiO_{3.87}$ composite ceramics sintered at $925^\circ C$ for 4 h.

Acknowledgments

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References

- [1] M.T. Sebastian, H. Jantunen, Low loss dielectric materials for LTCC applications: a review, *International Materials Reviews* 53 (2008) 57–90.
- [2] X.G. Wu, H. Wang, Y.H. Chen, D. Zhou, Synthesis and microwave dielectric properties of $Zn_3B_2O_6$ ceramics for substrate application, *Journal of the American Ceramic Society* 95 (2012) 1793–1795.
- [3] H.F. Zhou, X.L. Chen, L. Fang, X.B. Liu, Y.L. Wang, Microwave dielectric properties of $LiBiW_2O_8$ ceramics with low sintering temperature, *Journal of the American Ceramic Society* 93 (2010) 3976–3979.
- [4] W. Lei, W.Z. Lu, D. Liu, J.H. Zhu, Phase evolution and microwave dielectric properties of $(1-x)ZnAl_2O_4-xMg_2TiO_4$ ceramics, *Journal of the American Ceramic Society* 92 (2009) 105–109.
- [5] M. Guo, S.P. Gong, G. Dou, D.X. Zhou, A new temperature stable microwave dielectric ceramics: $ZnTiNb_2O_8$ sintered at low temperatures, *Journal of Alloys and Compounds* 509 (2011) 5988–5995.
- [6] K.P. Surendran, P.V. Bijumon, P. Mohanan, M.T. Sebastian, $(1-x)MgAl_2O_4-xTiO_2$ dielectric for microwave millimeter wave applications, *Applied Physics A* 81 (2005) 823–826.
- [7] Y. Lv, R.Z. Zuo, Structure and microwave dielectric properties of $Ba_3(VO_4)_2-Zn_{2-x}SiO_{4-x}$ ceramic composites, *Materials Research Bulletin*, submitted for publication.
- [8] R. Umeurua, H. Ogawa, A. Yokoi, H. Ohsato, A. Kan, Low-temperature sintering-microwave dielectric property relations in $Ba_3(VO_4)_2$ ceramic, *Journal of Alloys and Compounds* 424 (2006) 388–393.
- [9] N.H. Nguyen, J.B. Lim, S. Nahm, J.H. Paik, J.H. Kim, Effect of Zn/Si ratio on the microstructural and microwave dielectric properties of Zn_2SiO_4 ceramics, *Journal of the American Ceramic Society* 90 (2007) 3127–3130.
- [10] M.R. Joong, J.S. Kim, M.E. Song, S. Nahm, Formation and microwave dielectric properties of the $Mg_2V_2O_7$ ceramics, *Journal of the American Ceramic Society* 92 (2009) 1621–1624.

- [11] M.R. Joung, J.S. Kim, M.E. Song, J.H. Choi, J.W. Sun, S. Nahm, J.H. Paik, B.H. Choi, Effect of Li_2CO_3 addition on the sintering temperature and microwave dielectric properties of $\text{Mg}_2\text{V}_2\text{O}_7$ ceramics, *Journal of the American Ceramic Society* 92 (2009) 2151–2154.
- [12] S.H. Kweon, M.R. Joung, J.S. Kim, B.Y. Kim, S. Nahm, J.H. Paik, Y.S. Kim, T.Y. Sung, Low temperature sintering and microwave dielectric properties of B_2O_3 -added LiAlSiO_4 ceramic, *Journal of the American Ceramic Society* 94 (2011) 1995–1998.
- [13] A.Y. Borisevich, P.K. Davies, Effect of V_2O_5 doping on the sintering and dielectric properties of M-phase $\text{Li}_{1+x-y}\text{Nb}_{1-x-3y}\text{Ti}_{x+4y}\text{O}_3$ ceramics, *Journal of the American Ceramic Society* 87 (2004) 1047–1052.
- [14] S.P. Wu, J.H. Luo, S.X. Cao, Microwave dielectric properties of B_2O_3 -doped ZnTiO_3 ceramics made with sol–gel technique, *Journal of Alloys and Compounds* 502 (2010) 147–152.
- [15] H. Yamamoto, A. Koga, S. Shibagaki, N. Ichinose, Low temperature firing of MgTiO_3 – CaTiO_3 microwave dielectric ceramics modified with B_2O_3 or V_2O_5 , *Journal of the Ceramic Society of Japan* 106 (1998) 339–343.
- [16] H.T. Kim, S.H. Kim, S. Nahm, J.D. Byun, Y. Kim, Low-temperature sintering and microwave dielectric properties of zinc metatitanate–rutile mixtures using boron, *Journal of the American Ceramic Society* 82 (1999) 3043–3048.
- [17] N. Santha, M.T. Sebastian, Low temperature sintering and microwave dielectric properties of $\text{Ba}_4\text{Sm}_{0.33}\text{Ti}_{18}\text{O}_{54}$ ceramics, *Materials Research Bulletin* 43 (2008) 2278–2284.
- [18] G. Baret, R. Madar, C. Bernard, Phase equilibria diagrams, CD-ROM database version 3.1, The American Ceramic Society, Fig. 09273, 1991.
- [19] H. Zhuang, Z.X. Yue, F. Zhao, L.T. Li, Low-temperature sintering and microwave dielectric properties of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ – BaWO_4 composite ceramics for LTCC applications, *Journal of the American Ceramic Society* 91 (2008) 3275–3279.
- [20] W.E. Courtney, Analysis and evaluation of a method of measuring the complex permittivity and permeability of microwave insulators, *IEEE Microwave Theory and Techniques* 18 (1970) 476–485.
- [21] M.H. Whitmore, H.R. Verdun, D.J. Singel, Electron-paramagnetic-resonance spectroscopy of manganese-doped $\text{Ba}_3(\text{VO}_4)_2$: identification of tetrahedral Mn^{5+} and Mn^{4+} centers, *Physical Review B* 47 (1993) 11479–11482.
- [22] J.S. Kim, N.H. Nguyen, J.B. Lim, D.S. Paik, S. Nahm, J.H. Paik, J.H. Kim, H.J. Lee, Low-temperature sintering and microwave dielectric properties of the Zn_2SiO_4 ceramics, *Journal of the American Ceramic Society* 91 (2008) 671–674.
- [23] B.J. Jeong, M.R. Joung, S.H. Kweon, J.S. Kim, S. Nahm, J.W. Choi, S.J. Hwang, Effect of Bi_2O_3 doping on the sintering temperature and microwave dielectric properties of LiAlSiO_4 ceramics, *Journal of the American Ceramic Society* 95 (2012) 1811–1813.