Journal of Alloys and Compounds 639 (2015) 359-364



Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Microwave dielectric properties of (Mg_{0.4}Zn_{0.6})₂SiO₄–CaTiO₃ ceramics sintered with Li₂CO₃–H₃BO₃ for LTCC technology



ALLOYS AND COMPOUNDS



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ARTICLE INFO

Article history: Received 7 February 2015 Received in revised form 6 March 2015 Accepted 7 March 2015 Available online 14 March 2015

Keywords: (Mg_{0.4}Zn_{0.6})₂SiO₄-CaTiO₃ Composite ceramics Microwave dielectric properties LTCC

ABSTRACT

The effects of different adding methods of Li₂CO₃, H₃BO₃, Li₂CO₃-H₃BO₃ glass (B-Li glass) and Li₂CO₃-H₃BO₃ (LB) additives on the microstructure and microwave dielectric properties of 0.88 (Mg_{0.4}Zn_{0.6})₂SiO₄-0.12CaTiO₃ (MZS-C) ceramics were investigated. Of all the adding methods, the addition of LB is the most effective way to lower the sintering temperature of MZS-C ceramics with good microwave dielectric properties. With LB addition, the MZS-C ceramics can be well sintered below 950 °C. The phase formation, microstructure, chemical compatibility with silver and microwave dielectric properties of MZS-C composite ceramics with LB addition were also systematically studied. The dielectric constant and $Q \times f$ value were related to the amount of the LB addition. The MZS-C ceramics with 4.0 wt.% LB sintered at 950 °C/2 h exhibited excellent microwave dielectric properties of ε_r = 7.12, $Q \times f$ = 28,600 GHz and τ_f = -6 ppm/°C. Meanwhile, the material was compatible with silver, which made it a promising candidate material for LTCC application.

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1. Introduction

With the rapid development of high-frequency wireless communication technology over the past decades, extensive attention has been paid to the high quality microwave dielectric materials [1]. To meet the requirements of improving performances and realizing miniaturization and integration for microwave devices, low temperature co-fired ceramic (LTCC) technology emerged and has been widely investigated. For LTCC applications, the sintering temperature of microwave dielectric ceramics must be lower than the melting points of the metal electrodes, such as Ag (ca. 961 °C). Besides, the microwave dielectric materials should also have a high quality factor value ($Q \times f$), a near zero temperature coefficient of resonant frequency ($\tau_f \approx 0$ ppm/°C) and chemical compatibility with metal electrodes [2–4].

As important silicates, Mg₂SiO₄ and Zn₂SiO₄ have been investigated as potential microwave dielectric ceramics due to their low dielectric constants (6–7), high $Q \times f$ values (>200,000 GHz) and high chemical stability [5–7]. However, the large negative τ_f values (ca. –60 ppm/°C) and relatively high sintering temperature place constraints on their manufacture for use in practical applications. Song et al. [8] reported that the densification temperatures of $(Mg_{1-x}Zn_x)_2SiO_4$ ceramics were much lower than those of Mg₂SiO₄ and Zn₂SiO₄. (Mg_{0.4}Zn_{0.6})₂SiO₄ synthesized by solid-state reaction method sintered at 1250 °C possessed excellent dielectric properties: ε_r = 6.6, Q × f = 95,650 GHz, τ_f = -60 ppm/°C. In order to develop the τ_f value to zero, the most effective way to achieve temperature stable dielectric materials is to mix component materials with opposite τ_f values. Mg₂SiO₄-CaTiO₃ composite ceramics reported by Dou et al. [9] exhibited excellent microwave dielectric, and the $\tau_{\rm f}$ value was found to be dependent on phase constitution, which is related to the amount of CaTiO₃. Nevertheless, the sintering temperatures of MZS and CaTiO₃ are above 1100 °C, which are too high for LTCC application. In the research area of LTCC technology, low melting point oxides or fine glass powders were often used to lower the sintering temperature, such as CuO, B₂O₃, Bi₂O₃, Li₂O, and V₂O₅ [10,11]. The sintering temperature of forsterite (Mg₂SiO₄) ceramics could be lowered to 950 °C with addition of LBS glass and LMBZS glass, respectively [12,13]. Zhang et al. [14] reported that $(Zn_{0.8}Mg_{0.2})_2SiO_4$ -TiO₂ with 3 wt.% Li₂O-B₂O₃ attained successful sintering temperature at 900 °C.

The aim of our research is to decrease the sintering temperature of $0.88(Mg_{0.4}Zn_{0.6})_2SiO_4-0.12CaTiO_3$ (MZS-C) composite ceramics without obviously deteriorating its microwave dielectric properties. In the present work, MZS-C composite ceramics were

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prepared by a conventional solid-state method, by adding (1) Li_2CO_3 , (2) H_3BO_3 , (3) $Li_2CO_3-H_3BO_3$ glass (B-Li glass), and (4) $Li_2CO_3-H_3BO_3$ (LB), respectively. The low sintering temperature behavior, phase composition, microstructure, microwave dielectric properties and chemical compatibility with silver of this system were investigated to meet the requirement of microwave devices.

2. Experimental procedures

(Mg_{0.4}Zn_{0.6})₂SiO₄ and CaTiO₃ compounds were individually prepared by using the conventional solid-state reaction method using high-purity reagents. All the raw materials were first dried at 500 °C for 3 h to avoid any water and CO2 absorption. High-purity powders MgO (99.99%), ZnO (99.99%), SiO₂ (99.99%), CaCO₃ (99.99%) and TiO₂ (99.6%) were weighted according to the compositions $(Mg_{0.4}Zn_{0.6})_2SiO_4$ and CaTiO₃, and then were ball-milled in a polyethylene bottle with zirconia balls in distilled water for 24 h. After dried at 100 °C, the mixed powders were ground and then calcined at 1200 °C for 3 h in air. The compounds were subsequently ball-milled with Li₂CO₃ (99.99%) and H₃BO₃ (99.99%) for 24 h and dried again to obtain the desired compositions: 0.88(Mg_{0.4}Zn_{0.6})₂ SiO₄-0.12CaTiO₃ (MZS-C) with 4.0 wt.%, 5.0 wt.%, 6.0 wt.% and 7.0 wt.% Li₂ CO3-H3BO3 addition. Added with 5 wt.% PVA solution as a binder, the powders were pressed into cylindrical compacts of 10 mm in diameter and 6-7 mm in thickness at uniaxial pressure of 100 MPa. The compacts were firstly heated at 550 °C in air for 5 h to expel the organic binder, and subsequently sintered at 875–950 °C in air for 2 h.



Fig. 1. XRD patterns of the MZS-C ceramics with 5.0 wt.% different additions sintered at 950–1000 $^\circ C$ for 2 h in air.

The sintering aid B-Li glass was used in the study, and it was made from Li₂CO₃ and H₃BO₃ powders. 100 grams of mixtures with appropriate compositions were ball milled using zirconia balls in an ethanol medium for 12 h. The batch was then melted in a platinum crucible at 1000 °C for 4 h in air, followed by quenching to room temperature. The quenched glass was ball-milled in a nylon jar with zirconia balls for 12 h.

The experiment scheme was designed to study the effects of different adding methods on the microstructure and the microwave dielectric properties of the samples. The calcined MZS and CaTiO₃ powders doped with 5.0 wt.% Li₂CO₃, H₃BO₃, B-Li glass and Li₂CO₃–H₃BO₃ were mixed for 24 h with ZrO₂ ball and distilled water. And the pellets were sintered at 875–1000 °C in air for 2 h.

The samples were ground into powders, and the phase constitution was analyzed by using X-ray powder diffraction (XRD: Rigaku D/MAX, Cu Ka radiation, Japan). The microstructure was studied by using a field emission scanning electron microscopy (FESEM, XL30FEC, Philips, Netherlands). Composition analysis was performed by using energy dispersive X-ray spectrum (EDS) (Oxford INCA). Bulk densities of the sintered ceramics were measured by using the Archimedes method. Microwave dielectric properties were measured by using a network analyzer (Agilent, E5071C). Dielectric constant ε_r and $Q \times f$ values at microwave frequencies were measured by using the Hakki–Coleman dielectric resonator method [15]. Temperature coefficient of resonant frequency (τ_f) at microwave frequencies was measured over 25–80 °C. The τ_f value (ppm/°C) is calculated by using the equation:

$$\tau_f = \frac{f_{80} - f_{25}}{55 \times f_{25}} \times 10^6 \text{ ppm/}^{\circ} \text{C}, \tag{1}$$

where f_{80} and f_{25} are the resonant frequencies at 80 and 25 °C, respectively.

3. Results and discussions

Fig. 1 shows the X-ray diffraction patterns of the MZS-C ceramics with different additions sintered at 950–1000 °C for 2 h in air. The samples with only 5.0 wt.% Li₂CO₃ or H₃BO₃ could not be densified below 1000 °C/2 h. The MZS-C ceramics with the addition of B-Li glass or LB, however, were sintered successful below 950 °C/2 h. The XRD results clearly indicated that all samples contained three phases: Zn_2SiO_4 (ICDD-PDF #37-1485), Mg_2SiO_4 (ICDD-PDF #34-0189) and CaTiO₃ (ICDD-PDF #42-0423). Except for the H₃BO₃, the addition of other sintering aids (mainly Li₂CO₃) introduced other two phases $ZnTiO_3$ (ICDD-PDF #39-0190) and Ca₂SiO₄ (ICDD-PDF #52-0069), which may have an influence on the microwave dielectric properties of the samples.

The SEM micrographs of the MZS-C ceramics with 5.0 wt.% different additions sintered at 950–1000 °C for 2 h in air are shown in Fig. 2. Porous microstructures was observed in Fig. 2(a) and (b), which indicates that the MZS-C ceramics with the addition of only 5 wt.% Li₂CO₃ or H₃BO₃ could not be sintered densely at 1000 °C/



Fig. 2. SEM micrographs of the MZS-C ceramics with 5.0 wt.% (a) Li₂CO₃ at 1000 °C, (b) H₃BO₃ at 1000 °C, (c) B-Li glass at 950 °C and (d) Li₂CO₃-H₃BO₃ at 950 °C.

Table 1

Microwave dielectric properties of the MZS-C ceramics with 5.0 wt.% different additions sintered at 950–1000 $^\circ C$ for 2 h in air.

Additions (5.0 wt.%)	Sintering temperature (°C)	ε_r	$Q \times f$ (GHz)
Li ₂ CO ₃	1000	5.56	13,600
H ₃ BO ₃	1000	6.36	6200
B-Li glass	950	6.45	21,900
Li ₂ CO ₃ -H ₃ BO ₃	950	7.16	32,700



Fig. 3. Density and microwave dielectric properties of the MZS-C ceramics with 5.0 wt.% addition of B-Li glass and $Li_2CO_3-H_3BO_3$ sintered at 875–950 °C for 2 h in air.

2 h. Due to the liquid-phase effect, the dense microstructures and little pores were found in Fig. 2(c) and (d) compared with Fig. 2(a) and (b). More pores lead to the high dielectric loss, which is confirmed by the microwave dielectric measurement as shown in Table 1. The addition of B-Li glass or Li_2CO_3 –H₃BO₃ has an effect of lowering the sintering temperature dramatically, which also made the samples densified below 950 °C. The occurrence of fuzzy grain boundary in Fig. 2(c) indicated the presence of much glass phase, which may deteriorate the microwave dielectric properties.

Fig. 3 shows the density and microwave dielectric properties of the MZS-C ceramics with 5.0 wt% addition of B-Li glass and Li₂CO₃-H₃BO₃ sintered at 875–950 °C for 2 h in air. It can be seen that the densities of samples increased with increasing the sintering temperature and the samples with Li₂CO₃-H₃BO₃ possess higher density values than those of samples with B-Li glass. It is noted that the dielectric constant increased with increasing sintering temperature for the fixed compositions. Since density plays an important role in influencing the dielectric constant, ε_r value would increase with increasing density resulting in showing similar variation trend [16]. The $Q \times f$ values of samples with B-Li glass were nearly invariable with the increasing sintering temperature indicating that the samples were densely sintered over a large temperature range, which is consistent with the corresponding slight change of density. Unlike the addition of B-Li glass, the $Q \times f$ values of samples with Li₂CO₃-H₃BO₃ increased linearly with



Fig. 4. XRD patterns of the MZS-C ceramics with (a) 4.0 wt.%, (b) 5.0 wt.%, (c) 6.0 wt.% and (d) 7.0 wt.% $Li_2CO_3-H_3BO_3$ addition sintered at 950 °C for 2 h in air.

the increasing sintering temperature and exceeded those of samples with B-Li glass, which may be caused by the presence of much glass phase as shown in Fig. 2(c).

The XRD patterns of the MZS-C ceramics with 4.0–7.0 wt.% $Li_2CO_3-H_3BO_3$ addition sintered at 950 °C for 2 h in air were shown in Fig. 4. Its clearly observed that the main crystal phase is Zn_2SiO_4 accompanied by Mg_2SiO_4 , $CaTiO_3$ phases and other two phases $ZnTiO_3$ and Ca_2SiO_4 . With increasing LB content, obviously the peak intensity of $CaTiO_3$ is weakened and that of $ZnTiO_3$ is increased significantly. From the results in Figs. 1 and 4 it is concluded that the addition of Li_2CO_3 promotes the appearance of $ZnTiO_3$ phase.

SEM micrographs of the MZS-C ceramics with $Li_2CO_3-H_3BO_3$ sintered at different temperatures were shown in Fig. 5. A dense microstructure with hardly any porosity was observed from Fig. 5(c)–(f). With increasing sintering temperature, a microstructure with decreased porosity and increased grain size was observed from Fig. 5(a)–(d), which affected the density of the samples. The microstructure of samples gets denser with the increasing LB content, suggesting that the addition of LB could improve the sinterability and accelerate the shrinkage of the ceramics. Fig. 5(e) and (f) shows that more LB additions would result in the abnormal grain growth and more uneven grain size distribution.

Fig. 6 depicts the bulk densities of the MZS-C ceramics with 4.0-7.0 wt.% Li₂CO₃-H₃BO₃ addition sintered at 875-950 °C for 2 h in air. The density of samples increased with the increase of LB content at the same sintering temperature, which agreed well with the results of SEM images. Meanwhile, the density of samples increased gradually with the increasing sintering temperature at the fixed composition due to the decrease in the porosity and the increase of the grain size. Fig. 7 shows the dielectric constant of the MZS-C ceramics with 4.0-7.0 wt% Li₂CO₃-H₃BO₃ addition sintered at 875-950 °C for 2 h in air. The relationship between the ε_r and sintering temperature reveals the same trend as that between density and sintering temperature. It can be seen that ε_r increased with increasing content of LB at the same sintering temperature. This is because the samples reach fewer pores and larger grain size, which is evidenced in Fig. 5(d)–(f). The dielectric constant ε_r at the fixed composition was found to increase monotonically with increasing the sintering temperature due to the decrease in porosity.

Fig. 8 shows the $Q \times f$ values of the MZS-C ceramics with 4.0– 7.0 wt.% Li₂CO₃–H₃BO₃ addition sintered at 875–950 °C for 2 h in air. Generally, the $Q \times f$ values first increased and then decreased with increasing the LB content. The $Q \times f$ values reached a maximum value (32,700 GHz) sintered at 950 °C when 5.0 wt.% LB



Fig. 5. SEM micrographs of the MZS-C ceramics with *x* wt.% Li₂CO₃-H₃BO₃ addition: (a) x = 5.0 at 875 °C, (b) x = 5.0 at 900 °C, (c) x = 5.0 at 925 °C, (d) x = 5.0 at 950 °C, (e) x = 6.0 at 950 °C and (f) x = 7.0 at 950 °C.



Fig. 6. Bulk densities of the MZS-C ceramics with 4.0–7.0 wt.% $Li_2CO_3-H_3BO_3$ addition sintered at 875–950 $^\circ C$ for 2 h in air.





Fig. 7. Dielectric constant of the MZS-C ceramics with 4.0–7.0 wt.% $Li_2CO_3-H_3BO_3$ addition sintered at 875–950 °C for 2 h in air.

upon $Q \times f$ values of the samples. The $Q \times f$ values increased with increasing sintering temperature from 875 to 950 °C, which is mainly due to the decrease in porosity and increase in grain size. As seen in Fig. 5(a)–(d), the microstructure with decreased porosity and increased grain size was observed with increasing sintering temperature. The grains become larger when the sintering temperature increases, which will result in higher $Q \times f$ value, because the larger grains could lead to lower grain boundaries and dielectric loss [18].



Fig. 8. $Q \times f$ values of the MZS-C ceramics with 4.0–7.0 wt.% Li₂CO₃–H₃BO₃ addition sintered at 875–950 °C for 2 h in air.



Fig. 9. τ_f value of the MZS-C ceramics with 4.0–7.0 wt.% $Li_2CO_3-H_3BO_3$ addition sintered at 950 °C for 2 h in air.



Fig. 10. XRD patterns of (a) MZS-C ceramics with 4.0 wt.% Li₂CO₃-H₃BO₃ and 20.0 wt.% Ag powders addition (b) MZS-C ceramics with 4.0 wt.% Li₂CO₃-H₃BO₃ addition sintered at 950 °C for 2 h in air.

Fig. 9 shows the τ_f values of the MZS-C ceramics with 4.0– 7.0 wt.% Li₂CO₃-H₃BO₃ addition sintered at 950 °C for 2 h in air. It can be seen that the τ_f value tends to be shifted towards the



Fig. 11. Back scattered electronic image and corresponding EDS analysis of the MZS-C ceramics with 4.0 wt.% Li₂CO₃-H₃BO₃ and 20.0 wt.% Ag powders addition sintered at 950 °C for 2 h in air.

negative direction with the increasing LB content and varied from -6 ppm/°C to -43 ppm/°C. The impurity phases ZnTiO_3 and Ca_2SiO_4 was observed when the MZS-C ceramics were added with LB, and the content of ZnTiO_3 increased with the increasing LB addition. Consequently, the decrease in τ_f value may be related to the ZnTiO_3 and Ca_2SiO_4 phase. It indicated that the τ_f value of samples can be adjusted with the LB content.

The XRD patterns, back scattered electronic image and corresponding EDS analysis of the MZS-C ceramics with 4.0 wt.% Li₂CO₃-H₃BO₃ and 20.0 wt.% Ag powders addition were shown in Figs. 10 and 11, respectively. The chemical compatibility with silver was investigated by co-firing the MZS-C compounds with LB addition and pure Ag powders at 950 °C for 2 h in air. The XRD patterns show that the peaks of Ag were observed and no other impurity phases were detected, which reveals that no reaction occurred between the low-fired MZS-C ceramics and Ag electrodes. The isolated Ag particle was detected in Fig. 11, which agrees well with the results in Fig. 10. Therefore, the MZS-C composite material that exhibited chemical compatibility with silver was promising for LTCC application.

4. Conclusions

The addition of $Li_2CO_3-H_3BO_3$ is the most effective way to lower the sintering temperature of $0.88(Mg_{0.4}Zn_{0.6})_2SiO_4-0.12CaTiO_3$ ceramics with good microwave dielectric properties below 950 °C in contrast with other adding methods of Li_2CO_3 , H_3BO_3 and B-Li glass. The phase formation, microstructure and microwave dielectric properties are found to be strongly associated with the amount of Li₂CO₃-H₃BO₃ addition. With increasing of the LB content, the CaTiO₃ phase decreased and the impurity phase ZnTiO₃ increased significantly. As increasing the LB content, the densities and ε_r values of MZS-C ceramics increased gradually, the maximum $Q \times f$ value (32,700 GHz) was obtained when 5.0 wt.% LB was added sintered at 950 °C/2 h and the τ_f value shifted to the negative direction duo to the increasing ZnTiO₃ phase. Addition of 4.0 wt.% LB in MZS-C ceramics sintered at 950 °C for 2 h exhibited excellent microwave dielectric properties of ε_r = 7.12, Q × f = 28,600 GHz and $\tau_f = -6 \text{ ppm/}^{\circ}\text{C}$. Moreover, the material was compatible with Ag electrodes, which made it a promising candidate material for LTCC application.

Acknowledgements

This research was supported by the National Key Fundamental Research Program (No. 2009CB623302). The authors are thankful to Agilent Corporation for the measure of microwave dielectric properties.

References

- [1] R.J. Cava, J. Mater. Chem. 11 (2001) 54.
- [2] M. Valant, D. Suvorov, J. Am. Ceram. Soc. 83 (2000) 2721.
- [3] M.T. Sebastian, H. Jantunen, Int. Mater. Rev. 53 (2008) 57.
- A.K. Axelsson, N.M. Alford, J. Eur. Ceram. Soc. 26 (2006) 1933. [4]
- [5] H. Ohsato, T. Tsunooka, T. Sugiyama, K. Kakimoto, H. Ogawa, J. Electroceram. 17 (2006) 445.
- [6] T. Tsunooka, T. Sugivama, H. Ohsato, K. Kakimoto, M. Andou, Y. Higashida, H. Sugiura, Key Eng. Mater. 269 (2004) 199.
- [7] J.L. Zou, Q.L. Zhang, H. Yang, H.P. Sun, Jpn. J. Appl. Phys. 45 (2006) 4143.
- [8] K.X. Song, X.M. Chen, C.W. Zheng, Ceram. Int. 34 (2008) 917.
- [9] G. Dou, D.X. Zhou, M. Guo, S.P. Gong, Y.X. Hu, J. Mater. Sci.: Mater. Electron. 24 (2013) 1431.
- [10] J.S. Kim, M.E. Song, M.R. Joung, J.H. Choi, S. Nahm, S.I. Gu, J.H. Paik, B.H. Choi, J. Eur. Ceram. Soc. 30 (2010) 375.
- D. Pamu, G.L.N. Rao, K.C.J. Raju, J. Alloys Comp. 509 (2011) 9289.
 T.S. Sasikala, M.N. Suma, P. Mohanan, C. Pavithran, M.T. Sebastian, J. Alloys
- Comp. 461 (2008) 555. [13] T.S. Sasikala, C. Pavithran, M.T. Sebastian, J. Mater. Sci.: Mater. Electron. 21 (2010) 141.
- [14] Q.L. Zhang, H. Yang, J.L. Zou, J. Mater. Sci.: Mater. Electron. 20 (2009) 181.
- [15] B.W. Hakki, P.D. Coleman, I.R.E. Trans, Microwave Theory Tech. 8 (1960) 402.
 [16] Q. Ma, S.P. Wu, C. Jiang, J.H. Li, Ceram. Int. 39 (2013) 2223.
- [17] S.H. Yoon, G.K. Choi, D.W. Kim, S.Y. Cho, K.S. Hong, J. Eur. Ceram. Soc. 27 (2007) 3087.
- [18] S.J. Penn, N.M. Alford, A. Templeton, X.R. Wang, M.S. Xu, M. Reece, K. Schrapel, J. Am. Ceram. Soc. 80 (1997) 1885.