Journal of Alloys and Compounds 509 (2011) 4848–4853

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Preparation and properties of the barium borate glassy matrix composite materials containing fused silica and monoclinic zirconia

Song Chen*, Shuren Zhang, Xiaohua Zhou, Zhong Wen

School of Microelectronics and Solid State Electronics, University of Electronic Science and Technology of China, Chengdu 610054, People's Republic of China

ARTICLE INFO

Article history:
Received 4 November 2010
Received in revised form 22 January 2011
Accepted 27 January 2011
Available online 23 February 2011

Keywords:
LTCC
Barium borate
Sintering
Dielectric properties
Fused silica
Zirconia

ABSTRACT

In this work, the LTCC composite materials containing fused silica and monoclinic zirconia ceramic particles, respectively, which based on the composite matrix composed of the barium borate glassy matrix and α-alumina ceramic particles, were prepared by traditional solid-state preparation process at a sintering temperature of 900 °C. Sintering mechanism and physical properties, e.g. dielectric properties and coefficient of thermal expansion (CTE), of the LTCC composite ceramics are investigated and discussed in detail in terms of their mineral phase composition. The results indicate that a barium borate glassy phase can be easily formed from a barium borate compound, which is obtained by the chemical combination of barium hydroxide octahydrate and an aqueous solution of boric acid, at a sintering temperature of 900 °C. In turn, the barium borate glassy melts can supply a liquid phase sintering aid for the fabrication of the LTCC composite ceramics with the sintering temperature of 900 °C during sintering. The introduction of the α-alumina ceramic particles to the barium borate glassy matrix can improve the sintering behavior whereas the presence of fused silica or monoclinic zirconia particles in the composite ceramics is important to adjust the dielectric, thermal and mechanical properties of the LTCC composite materials. The work may be referenced for the fabrication of multi-layer LTCC structures with tailored physical properties.

1. Introduction

Low temperature co-fired ceramic (LTCC) is a well-established multi-layer technology that has the ability to embed passive elements, such as resistors, capacitors and inductors into the ceramic package minimizing the size of the completed module [1]. Nowadays, with further miniaturization of electronic devices, the LTCC materials with excellent physical properties, such as dielectric, mechanical and thermal properties need to be developed to satisfy the requirements of high signal propagation speed and high reliability [2]. In particular, the LTCC materials can be fired with low melting conductors such as sliver (M.P. 961 °C) [3]. In most of LTCC materials used presently, glass-ceramics and glass/ceramic composites are widely applied to LTCC multi-layer structures due to their low sintering temperature and tailored physical properties [4,5]. Nevertheless, the manufactures of glass-ceramics are generally complex processes including preparations and diversifications of glass materials. The cost is also relatively high. Consequently, it should be considered by choosing more convenient and efficient methods to fabricate LTCC materials. It is well known that barium borate can be used usually to decrease the densification temperature of ceramic materials as a flux agent due to its low-melting characteristics (United States Patent: P.N. 4,897,249 and P.N. 4,931,133). Accordingly, barium borate can also be used to fabricate LTCC composite ceramics as a LTCC matrix [6,7], since the appropriate $BaO–B_2O_3$ compositions have the potential to transform into a glassy form at a relative low sintering temperature (800–900 °C) [8,9]. Especially in order to achieve a densification sintering, the introduction of the α-alumina ceramic particles to the barium borate glassy matrix can offer more possibilities to set a proper sintering behavior and maximize mechanical strength [10–14]. With this understanding, the composite matrix (BBA) of the barium borate glassy matrix and the α-alumina ceramic particles can be well combined with other functional ceramic particles and consequently achieve tailored physical properties and dense microstructure. In the present work, we try to examine dielectric, thermal and mechanical properties of the dense LTCC composite materials containing fused silica particles and monoclinic zirconia particles, respectively. Fused silica is a high purity synthetic amorphous silicon dioxide that combines a very low thermal expansion coefficient and therefore is resistant to thermal shock, whereas monoclinic zirconia is a stable form of zirconia and has good mechanical properties. The introduction of two ceramic particles to the BBA matrix is to develop the LTCC composite ceramics with low thermal expansion coefficient and good mechanical properties. Accordingly, sintering behavior and physical properties of the

---

* Corresponding author. Tel.: +86 28 83208048.
E-mail address: chengdu20100@163.com (S. Chen).

0925-8388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2011.01.188

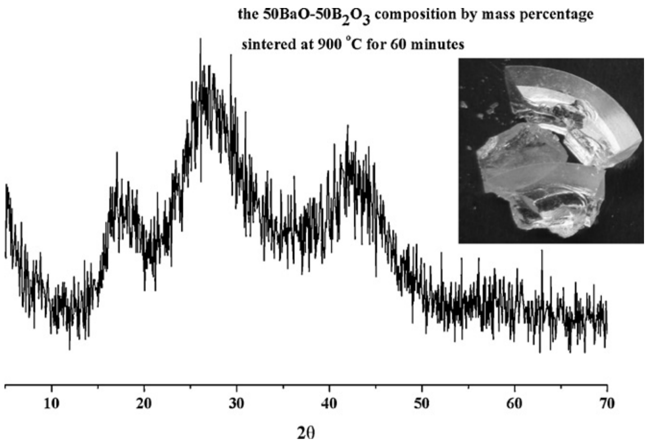

Fig. 1. The XRD pattern and the picture of the resulting product of the specimen BB sintered at 900 °C for 60 min.

composite ceramics are investigated in terms of their chemical compositions.

2. Experimental

Reagent-grade raw materials of boric acid, barium hydroxide octahydrate, α-alumina, fused silica and monoclinic zirconia with purity higher than 99% were used as the starting materials. According to the designed chemical composition of the matrix specimens in Table 1, the above starting materials were weighed and milled with de-ionized water for 12 h. The ratio of the water to solid was regulated to 3:1. Upon treatment, the slurries were dried and then pre-sintered at 700 °C for 3 h. In turn, the composite ceramics powders were made by mixing the pre-sintered BBA matrix powders with fused silica powders and monoclinic zirconia powders, respectively, and then by milling them in an alcohol medium for 12 h. Subsequently, all treated powders with the particle size of 0.5–1.0 μm were molded into green bodies (disc and bar) under a compressive stress of 20 MPa. Finally, the specimens were obtained by continuously sintering the green bodies at 400 °C for 3 h and 900 °C for 20 min. The as-sintered specimens were analyzed by using an X-ray powder diffraction patterns (D/Max-IIIA, Rigaku Industrial Corporation, Japan), a scanning electron microscope (Philips, FEI INSPECT F, U.S.A.) and a differential scanning calorimetry (NETZSCH STA449C, Germany, heating at a rate of 10 °C min^{-1}). X-ray powder diffraction patterns were recorded on a D/Max-IIIA machine (Rigaku Industrial Corporation, Japan) using Cu Kα Radiation (40 kV, 30 mA) with a scanning rate of 2° min^{-1} from 5° to 70° (2θ). Coefficient of thermal expansion (CTE) of the specimens was tested (in the temperature range of 25–400 °C) by a dilatometer (NETZSCH DIL402PC, Germany, heating at a rate of 3 °C min^{-1}). Dielectric properties were tested (1 MHz, at room-temperature) by a Precision LCR Meter instrument (Agilent 4284A, U.S.A.).

3. Results and discussion

Due to low melting characteristics, barium borate is widely used to decrease the densification sintering temperature of ceramic materials as a flux agent. According to the phase diagram of the binary system BaO–B$_2$O$_3$ [8,9], the onset of a liquid phase in the binary system BaO–B$_2$O$_3$ can be observed at least 869 °C. Specially, in the phase diagram of the binary system BaO–B$_2$O$_3$, a low temperature liquid-phase zone is located at a composition range of about 50–70 mol.% B$_2$O$_3$ content, which consequently supplies a reference for the design of the barium borate glassy matrix with low melting characteristics. Furthermore, considering the volatility of B$_2$O$_3$, the B$_2$O$_3$ content of the BaO–B$_2$O$_3$ composition designed in the work is inclined to a high level in the low temperature liquid-phase zone. A convenient method to obtain barium borate compounds (United States Patent: P.N. 4,897,249) is to chemically combine barium hydroxide octahydrate with an aqueous solution of boric acid. In the method, the barium borate glassy forms can be easily obtained by heating the hydrated barium borate, which has been designed in terms of the composition located at the low tem-

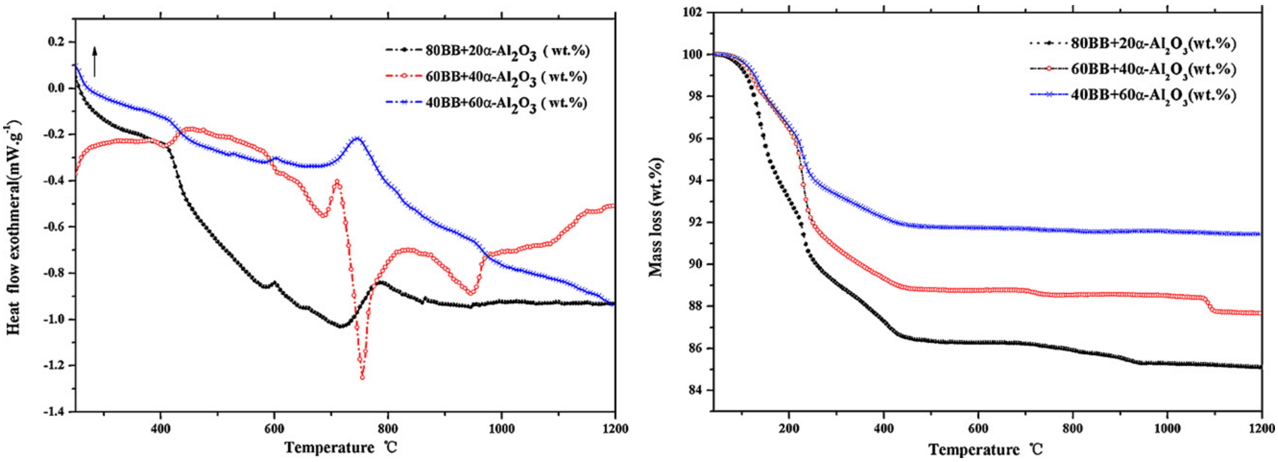

Fig. 2. The DSC-TG curves of the BBA matrixes with different dosage of the α-alumina ceramic particles.

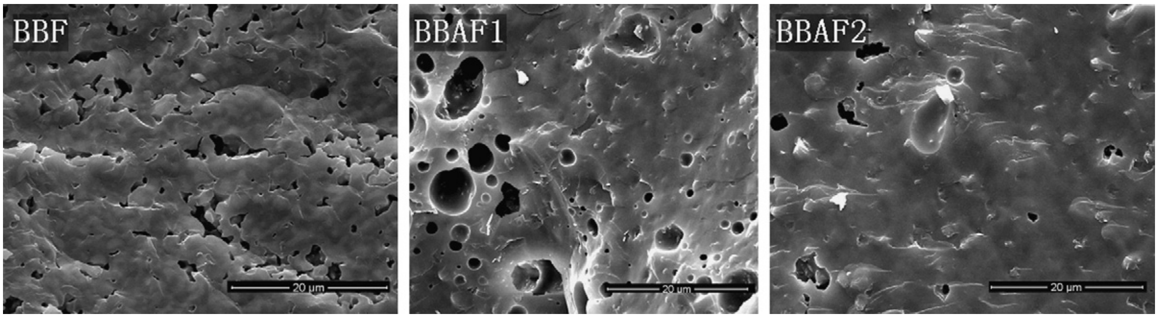

Fig. 3. The cross-section SEM of the specimens BBF, BBAF1 and BBAF2.

Table 1
The chemical composition of the matrixes and the composite ceramics.

Name	Specimen	Composition (wt.%)	Composition (mol.%)
Matrixes	BB	$50BaO–50B_2O_3$	$32BaO–68B_2O_3$
	BBA	60BB + 40α-Al_2O_3	62BB + 38α-Al_2O_3
	BBF	40BB + 60 fused silica	29BB + 71 fused silica
	BBZ	60BB + 40 monoclinic zirconia	66BB + 34 monoclinic zirconia
Composite ceramics	BBAF1	50BBA + 50 fused silica	34BBA + 66 fused silica
	BBAF2	40BBA + 60 fused silica	29BBA + 71 fused silica
	BBAZ1	80BBA + 20 monoclinic zirconia	84BBA + 16 monoclinic zirconia
	BBAZ2	60BBA + 40 monoclinic zirconia	66BBA + 34 monoclinic zirconia
	BBAZ3	50BBA + 50 monoclinic zirconia	56BBA + 44 monoclinic zirconia

perature liquid-phase zone in the diagram of the binary system $BaO–B_2O_3$. Fig. 1 shows the XRD patterns and the picture of the specimen BB with a $50BaO–50B_2O_3$ composition by mass percentage, which has been obtained by the above preparation method plus a 60 min sintering process at 900 °C. As shown on the pictures, it can be seen that the $BaO–B_2O_3$ composition treated at 900 °C has basically transformed into a glassy form, indicating that the binary $BaO–B_2O_3$ composition has the potential to fabricate the low-temperature sintering composite ceramics as a sintering agent. On the other hand, it is believed that the α-alumina ceramic particles with the optimal addition to most of LTCC materials, typically ranging from 30 to 50 wt.%, is known to further maximize mechanical strength and improve sintering behavior of composite ceramics. Fig. 2 gives the DSC-TG curves of the BBA matrixes with different dosage of the α-alumina ceramic particles. As shown on the DSC-TG curves, an obvious chemical effect between the barium borate glassy matrix and the α-alumina ceramic particles can be observed at the specimen BBA with 40 wt.% alumina additions at about 760 °C. It is estimated that the endothermic peak at about 760 °C is caused by the dissolution or the eutectic of the alumina ceramic particles to barium borate melts, which can offer more possibilities to improve the sintering behavior of the LTCC composite materials. In addition, it is found that the total mass loss of the three specimens is increasing with the increase of the B_2O_3 content in BBA matrix, suggesting that the volatility of an excessive B_2O_3 in the composition is occurring during sintering. Based on the BBA matrix with low melting characteristics, fused silica or monoclinic zirconia particles can be introduced to the BBA matrix and consequently fabricate the LTCC composite materials with tailored physical properties. Fused silica is a high purity synthetic amorphous silicon dioxide, which is characterized by a low thermal expansion coefficient and a low permittivity. Therefore, the addition of the fused silica particles to the BBA matrix is helpful to achieve the preparation of the LTCC materials with a low permittivity and a low thermal expansion coefficient, which can be well applied to the packages of semiconductor devices.

In order to investigate the sintering behavior of the LTCC composite materials containing fused silica particles, Fig. 3 shows the cross-section SEM of the specimens BBF, BBAF1 and BBAF2. As shown on the SEM of the three specimens, the porosity in the specimens BBF and BBAF1 are higher than that in the specimen BBAF2, indicating that the addition of the alumina ceramic particles to the barium borate glassy matrix can availably improve the microstructure of the fused silica composite ceramics. Also, the high content of the BBA matrix in the composite ceramics can also lead to the occurrence of the porosity due to the thermal swelling of the superfluous melting phase during sintering. Fig. 4 gives the XRD patterns of the matrixes and the composite ceramic specimens containing fused silica particles. It shows that, besides the formation of small aluminum barium compounds in the BBA matrix, the introduction of the alumina ceramic particles to the barium borate glassy does not obviously change the original constituent of the matrix, whereas the fused silica particles dispersing to the BBA matrix also does not result in the appearance of the second phase. Therefore, the chemical reaction activity between the matrices and the inclusions is lower. As a result, the fabrication of the LTCC composite materials based on the combination of the BBA matrix and fused silica particles can be well achieved. The other ceramic particles added to the BBA matrix, zirconia, is a very important industrial ceramic for structural applications because of its high toughness, which has proven to be superior to other ceramics. The thermodynamically stable, room temperature form of zirconia is monoclinic zirconia [15], which are widely applied to improve the mechanical properties of ceramics materials such as toughness and bending strength [16–18]. In the present work, the introduction of monoclinic zirconia to the BBA matrix is expected to develop the LTCC composite materials with good mechanical properties. Similarly, dielectric properties and thermal expansion coefficient need to be concerned. Fig. 5 represents the cross-section SEM of the specimens BBZ, BBAZ1, BBAZ2 and BBAZ3. As shown on the micrographs of the specimens, it is found that the specimens BBZ and BBAZ1, which contain 40 wt.% and 20 wt.% monoclinic zirconia, respectively, have undergone a serious over-firing during sintering whereas the specimens BBAZ2 and BBAZ3 have more dense microstructures. The results indicate that the introduction of the alumina ceramic particles to the BB matrix can availably improve the microstructure of the zirconia composite ceramics but the high content of the BBA matrix in the composite ceramics can also result in the occurrence of an over-firing. Additionally, the microstructure of the specimen BBAZ2 is denser than that of the specimen BBAZ3, implying that the low content of the BBA matrix in the composite ceramics cannot supply sufficient liquid phase to help the achievement of the densification sintering so as to remain more porosity in the specimen. Fig. 6 gives the XRD patterns of the composite ceramics containing monoclinic zirconia. According to the XRD pattern of the specimen BBZ, it is found that the monoclinic zirconia can be

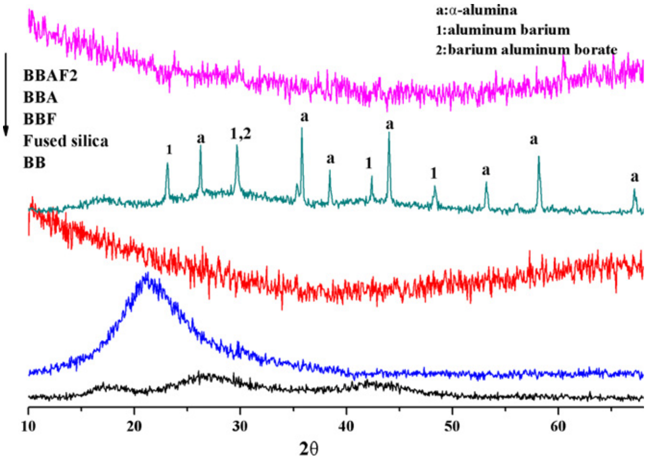

Fig. 4. The XRD patterns of the matrixes and the composite ceramic specimens containing fused silica particles.

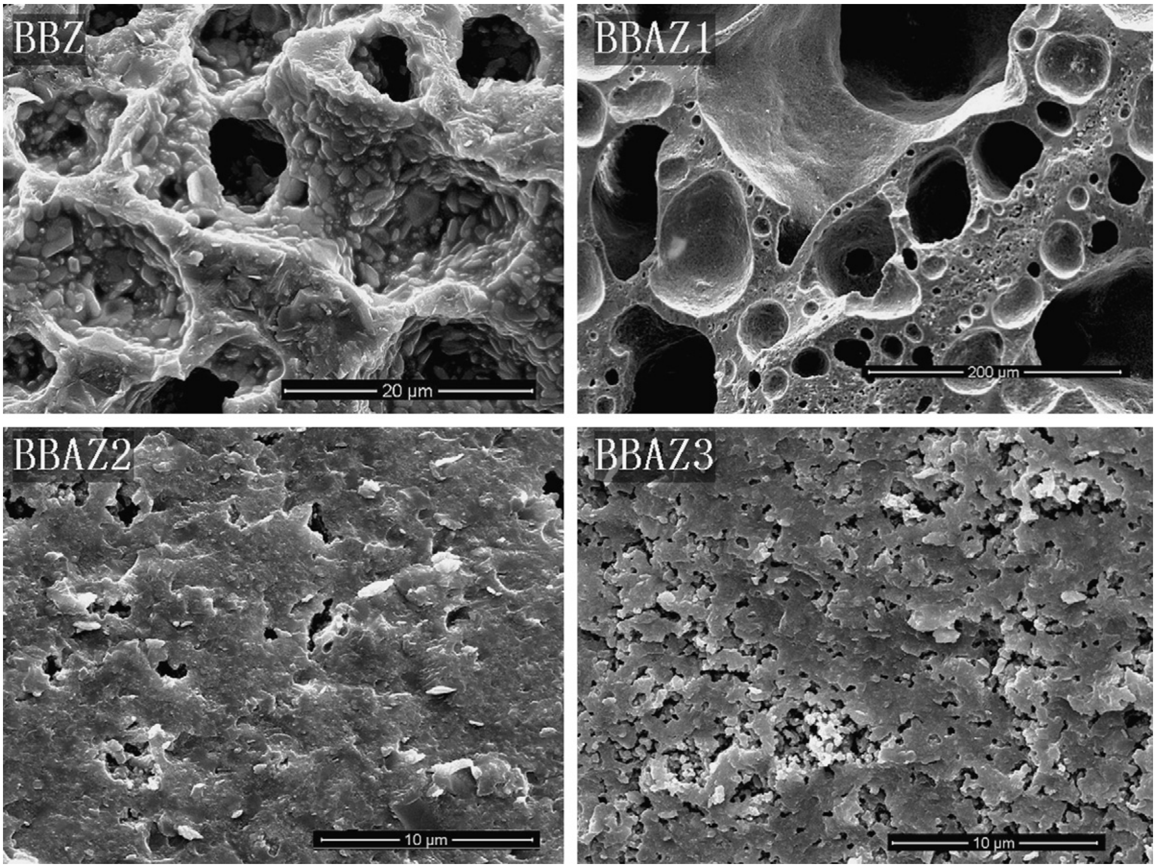

Fig. 5. The cross-section SEM of the specimens BBZ, BBAZ1, BBAZ2 and BBAZ3.

dissolved to the BB glassy matrix and consequently urge the formation of a $BaZr(BO_3)_2$ compound. In contrast to the specimen BBZ, the introduction of the monoclinic zirconia particles to the BBA matrix does not obviously result in the formation of new compounds. The results could be correlative to the relative low content of BB matrix in the specimens BBAZ2 and BBAZ3, consequently the monoclinic zirconia particles can stably exist in the BBA matrix. In consequence, the fabrication of the LTCC composite materials based on the combination of the BBA matrix and monoclinic zirconia particles can also be well achieved.

The physical properties, e.g. dielectric and thermal properties, of LTCC materials are mainly determined by the physical characteristics of their major mineral phases and the microstructures. In order to examine the correlation between the physical properties and the microstructures and mineral phases, a series of the tests for the dielectric properties and the thermal properties are carried out and the results are represented in Figs. 7–9, respectively. As shown in Fig. 7, the thermal expansion curves of several composite ceramics dependence of temperature (25–400 °C) are basically closed to a linear rule, indicating that the composite ceramics have stable thermal properties. The CTE of the composite ceramic specimens is

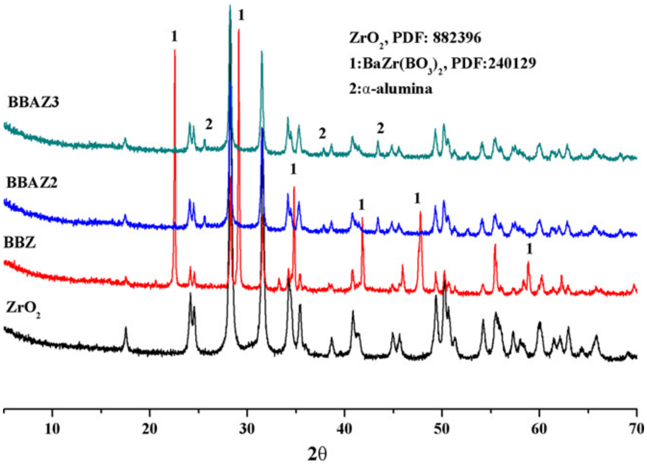

Fig. 6. The XRD patterns of the composite ceramic specimens containing monoclinic zirconia.

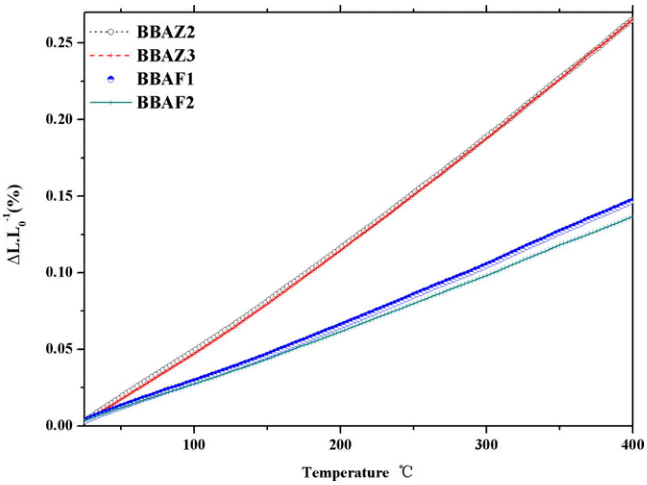

Fig. 7. The thermal expansion curves of the composite ceramics.

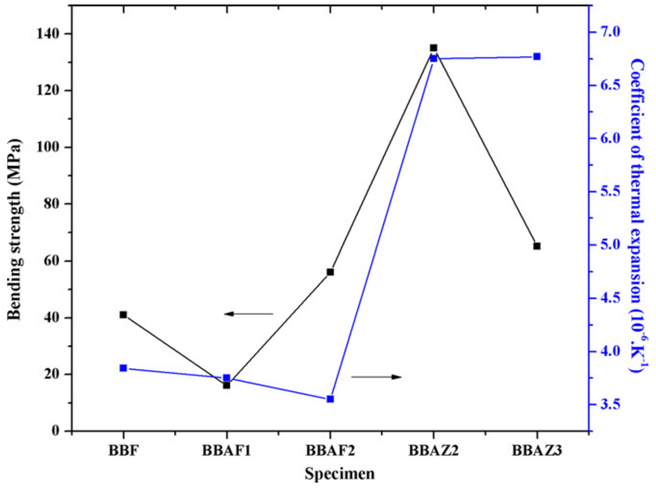

Fig. 8. The CTE and the bending strength of the composite ceramics.

given in Fig. 8. It shows that the specimens BBAF1 and BBAF2 have the CTE of about 3.5–3.8 ppm °C^{-1} whereas the specimens BBAZ2 and BBAZ3 have a moderate CTE (about 6.7–6.8 ppm °C^{-1}). Fig. 9 gives the dielectric properties of the composite ceramic specimens; it shows that the permittivity of the zirconia composite ceramics is totally higher than that of the fused silica composite ceramics. According to the literatures [19,20], the CTE and the permittivity of the fused silica glasses are 0.5 ppm °C^{-1} (0–200 °C) and 3.91 (at 1 kHz), respectively, whereas the CTE and the permittivity of zirconia ceramics are 10 ppm °C^{-1} and 22 (at 1 MHz), respectively. It can be estimated that the low CTE and permittivity of the specimens BBAF1 and BBAF2 should be originated from the physical characteristics of the fused silica. Also, the zirconia ceramic particles, as an inclusion, similarly have a great influence on the physical properties of the specimen BBAZ2 and BBAZ3. In fact, the correlations between the compositions of the composite ceramics and the CTE as well as the permittivity can be expressed approximately by Eq. (1) [20] and *Maxwell-Wagner* equation (2), respectively.

$$\alpha = \alpha_1 + \frac{(\alpha_2 - \alpha_1)V_2E_2(1-2\nu_1)}{V_1E_1(1-2\nu_2) + V_1E_1(1-2\nu_1)} \qquad (1)$$

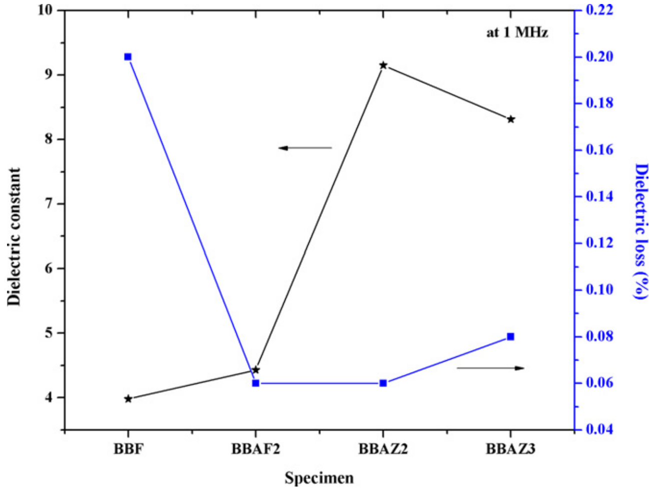

Fig. 9. The dielectric properties of the composite ceramics.

where α is the CTE, V the volumetric content, E the elasticity modulus, ν the poisson's ratio, and 1 and 2, the matrix, inclusions

$$\varepsilon_f = \varepsilon_h \frac{2\varepsilon_h + \varepsilon_l + 2V_l(\varepsilon_l - \varepsilon_h)}{2\varepsilon_h + \varepsilon_l - V_h(\varepsilon_l - \varepsilon_h)} \qquad (2)$$

where ε is the permittivity, V the volumetric content, and h and l, the phase with a high permittivity, the phase with a low permittivity.

Although Eqs. (1) and (2) give the calculation expresses for the CTE and the permittivity of a mixture of two phases, the physical properties of the composite ceramics with multi-phases are still depended mainly on their major phases. Therefore, the CTE and the permittivity of the LTCC composite materials containing fused silica and monoclinic zirconia particles are still controlled by the physical characteristics of the inclusions and their content in the composite ceramics. It is observed that, due to the content of the inclusions in the composite ceramics, the CTE of the specimen containing 60 wt.% fused silica (BBAF2) is lower than that of the specimen containing 50 wt.% fused silica (BBAF1). On the other hand, the microstructures of the composite ceramics have a great influence on the mechanical properties. The bending strengths of the composite ceramic specimens are given in Fig. 8. It is found that the mechanical properties of the zirconia composite ceramics are better than that of the fused silica composite ceramics. Especially, the specimen BBAZ2 has the highest bending strength in all specimens (up to 135 MPa). The excellent mechanical properties of the zirconia ceramics are responsible for the good mechanical properties of the zirconia composite ceramics. However, the bending strength of the specimen BBAZ3, which contains more the zirconia ceramic particles than the specimen BBAZ2, is lower than that of the specimen BBAZ2. It is believed that the deterioration of the mechanical properties of the specimen BBAZ3 resulted from the existence of the porosity in the specimen. The emergence of the remaining porosity in the specimens can be explained by the fact that the amount of the liquid phases is too small to fill all pores. In turn, the existence of the porosity in the specimen can also influence on the other physical properties such as dielectric properties.

In general, the present method in this work to fabricate the LTCC composite ceramics is very convenient by the combination of the ceramic particles with peculiar physical characteristics and the matrix with low melting characteristics. Especially, the physical properties of the composite ceramics can be designed and tailored availably in terms of the peculiar physical characteristics of the inclusions whereas the densification sintering can also be achieved without the addition of glass materials.

4. Conclusions

In the present work, we have successfully fabricated the composite ceramics with multi-phases by traditional solid-state preparation process at a sintering temperature of 900 °C. It is believed that the hydrated barium borate with an appropriate B_2O_3 content, which is located at a low temperature liquid-phase area in the binary BaO–B_2O_3 diagram, can transform into a glassy form at least 900 °C. It, consequently, can availably supply a liquid phase sintering aid for the fabrication of the LTCC composite ceramics with the sintering temperature of 900 °C. In addition, the introduction of the α-alumina ceramic particles to the barium borate glassy matrix can improve the sintering behavior and the microstructures of the composite ceramics. On the conditions, the addition of fused silica particles to the composite ceramics can achieve excellent dielectric properties (permittivity: 4.43 dielectric loss: 6×10^{-4}) and low thermal expansion (about 3.5–3.8 ppm °C^{-1}), whereas the introduction of the monoclinic zirconia particles to the composite ceramics can achieve a considerable bending strength (135 MPa) and good dielectric properties. The composite ceramics with tailored physical properties may be referenced for the application of multi-layer LTCC structures.

References

[1] Y. Imanaka, Multilayered Low Temperature Co-fired Ceramics (LTCC) Technology, Springer, New York, 2005, pp. 1–16.
[2] C. Jin, S. Lin, J.T. Wetzel, J. Electron. Mater. 30 (2001) 284–289.
[3] S.B. Lee, I. Kim, T.S. Park, Int. J. Fract. 150 (2002) 91–104.
[4] R. Wang, J. Zhou, B. Li, L. Li, J. Alloys Compd. 490 (2010) 204–207.
[5] G.-H. Chen, L.-J. Tang, J. Cheng, M.-H. Jiang, J. Alloys Compd. 478 (2009) 858–862.
[6] S. Chen, S. Zhang, X. Zhou, T. Zhang, M. He, J. Alloys Compd. 498 (2010) 185–190.
[7] S. Chen, X. Zhou, S. Zhang, B. Li, T. Zhang, J. Alloys Compd. 505 (2010) 613–618.
[8] A.B. Meshalkin, A.B. Kaplun, Bull. Mater. Sci. J. Cryst. Growth 275 (2005), e301-e305.
[9] E.M. Levin, H.F. McMurdie, F.P. Hall, Phase Diagrams for Ceramists, Columbus, The American Ceramic Society, 1956, p. 45.
[10] M.A. Vartanyan, E.S. Lukin, N.A. Popova, Glass Ceram. 65 (2008) 1–2.
[11] H.J. Kim, S.M. Nam., J. Ceram. Process. Res. 10 (2009) 817–822.
[12] Y.F. Zhang, S.L. Bai, M. Miao, Y.F. Jin, J. Eur. Ceram. Soc. 29 (2009) 1077–1082.
[13] C. Aksel, Mater. Lett. 57 (2002) 708–714.
[14] I.J. Choi, Y.S. Cho, J. Electroceram. 23 (2009) 185–186.
[15] J.K. Dewhurst, J.E. Lowther, Phys. Rev. B 57 (2) (1998) 741–747.
[16] J.C. Debsikdar, O.S. Sowemimo, J. Mater. Sci. 27 (1992) 5320–5324.
[17] H. Ruf, A.G. Evans, J. Am. Ceram. Soc. 66 (1983) 328–332.
[18] F.A.C. Oliveira, J.C. Fernandes, Ceram. Int. 28 (2002) 79–91.
[19] M. Brinkmann, J. Hayden, M. Letz, S. Reichel, et al., Springer Handbook of Lasers and Optics, Part A, Springer, New York, 2007, pp. 303–349.
[20] M. Eberstein, C. Glitzky, M. Gemeinert, T. Rabe, W.A. Schiller, Int. J. Appl. Ceram. Technol. 6 (2009) 1–8.