J. Am. Ceram. Soc., 95 [6] 1793–1795 (2012)
DOI: 10.1111/j.1551-2916.2012.05192.x

journal

Synthesis and Microwave Dielectric Properties of $Zn_3B_2O_6$ Ceramics for Substrate Application

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A novel microwave dielectric ceramics of $Zn_3B_2O_6$ for substrate application with low sintering temperature was synthesized by the solid-state reaction method. The sintering temperature ranges from 875°C to 950°C. The best microwave dielectric properties were obtained in the ceramic sintered at 925°C for 4 h with a permittivity ~6.7, a $Q \times f$ value about 58, 500 GHz and a temperature coefficient value of −58 ppm/°C. From the X-ray diffraction, backscattered electron imaging results of the co-fired sample with 20 wt% silver additive, the $Zn_3B_2O_6$ ceramic was found not to react with Ag at 950°C. The microwave dielectric properties and low sintering temperature of $Zn_3B_2O_6$ ceramic make it a promising candidate for Low temperature co-fired ceramic applications as substrate.

I. Introduction

In the past few decades, with the rapid development of modern microwave communication systems, such as mobile systems, high quality microwave dielectric ceramics have attracted more and more scientific and commercial attention. Low temperature co-fired ceramic (LTCC) technology and devices have been widely investigated for the use of reducing device size.[1–4] In the case of microwave substrate application and higher frequency applications (such as millimeter wave or higher), low dielectric constant (low-K) less than 10 are ideal values for integrated circuits. In addition, the microwave dielectric materials are required to have high quality value (low loss tangent) and a near-zero temperature coefficient of resonant frequency. The microwave dielectric ceramics used for LTCC technology must be chemically compatible with the conducting electrode materials, such as silver, copper etc., and possess a lower sintering temperature than the melting points of Ag or Cu (960°C and 1083°C, respectively).[5–7]

Some kinds of low-K materials with intrinsic low sintering temperature have been investigated for LTCC application. Bang reported that $MgCo_2(VO_4)_2$ ceramic synthesized by a sol–gel method sintered at 930°C for 5 h has a ε_r of 10.34, and a $Q \times f$ of 55 740 GHz.[8] Valant *et al.* investigated the sintering performance and dielectric characterization of some tellurite ceramics such as $TiTe_3O_8$, $Bi_2Te_2O_8$, Bi_2TeO_6 and $Bi_6Te_2O_{15}$.[9,10] Ratheesh *et al.* reported that $MgTe_2O_5$ ceramics were sintered in the temperature range of 640°C–720°C with ε_r = 10.5, $Q \times f$ = 61 000 GHz, and TCF = −45 ppm/K. The $BaCe_2(MoO_4)_4$ ceramic with ε_r = 12.3, Q = 3320 and TCF = −37 ppm/K has a low sintering temperature about 835°C.[11,12] Although these compounds have low sintering temperatures, their dielectric constants were a little higher for substrate application and the tellurite ceramics react with Ag electrode. Hence, searching for new material systems with low sintering temperatures and good microwave dielectric properties always attracts much interest.

Došler *et al.* reported the synthesis and dielectric characteristics of $Mg_3B_2O_6$. Although the ceramic has low permittivity (~7) and high Qf value (>220 000 GHz), its sintering temperature is too high (>1200°C) to LTCC technology.[13,14] The structural properties of $Zn_3B_2O_6$ have been reported earlier.[15,16] It belongs to a monoclinic structure with space group C2/c. In the present article, we report the microwave dielectric properties of the $Zn_3B_2O_6$ ceramic and its synthesis with low sintering temperature for the first time.

II. Experimental Procedure

The $Zn_3B_2O_6$ ceramics were prepared by conventional solid-state reaction techniques. High purity ZnO (>99.0%; Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) and H_3BO_3 (≥99.5%; Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) were used as starting materials for the synthesis of zinc borate. For the loss of B_2O_3 which occurred during the pre-reactions of $Zn_3B_2O_6$, 15 wt% excess of H_3BO_3 for the stoichiometric compensation. Then the above raw materials were milled in acetone medium using zirconia balls for 4 h. The slurry was dried at 120°C in hot air oven and calcined at 800°C for 4 h. The calcined powders were then milled again, dried, and sieved with 120 meshes. A quantity of 5 wt% polyvinyl alcohol (PVA) was added into the sieved powders and this was granulated with 60 meshes and then uniaxially pressed into pellets with 12 mm diameter and 5 mm thickness under the pressure of about 150 MPa. Then the $Zn_3B_2O_6$ ceramic pellets were sintered at 875°C–975°C for 4 h in air.

The crystal structures of the samples were analyzed by powder X-ray diffraction (XRD) using an X-ray diffractometer (D/MAX-2400; Rigaku, Tokyo, Japan) with CuK_α radiation generated at 40 kV and 100 mA. The microstructure observation of the samples was performed using scanning electron microscopy (SEM) (JSM-6460LV; JEOL, Tokyo, Japan). The precipitated phases in ceramics were observed using backscattered electron imaging (BEI) coupled with energy dispersive X-ray spectroscopy (EDS). The bulk densities of the sintered samples were measured using Archimedes method with distilled water. Dielectric behaviors in microwave frequency were measured by the $TE_{01\delta}$-shielded cavity method[17], using a Network Analyzer (8720ES; Agilent, Palo Alto, CA) and a temperature

D. Suvorov—contributing editor

Manuscript No. 30877. Received December 30, 2011; approved March 04, 2012.
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chamber (Delta 9023; Delta Design, Poway, CA). The permittivity and dielectric losses (tan δ) were calculated using the software provided by the $TE_{01\delta}$ shielded cavity supplier (Resonant cavity; QWED, Warsaw, Poland). The Q values were calculated from the tan δ values in accordance with the equation $Q = 1/\tan\ \delta$. The temperature coefficients of resonant frequency τ_f values were calculated using the formula $\tau_f = (f_T - f_0)/f_0(T - T_0)$ where f_T, f_0 were the resonant frequencies at the measuring temperature T and T_0 (25°C), respectively.

III. Results and Discussion

The XRD result, SEM micrographs of the surface, and cross section of $Zn_3B_2O_6$ ceramic sintered at 925°C for 4 h are shown in Fig. 1. The XRD patterns of $Zn_3B_2O_6$ ceramic sintered at this temperature can be well indexed as a pure monoclinic structure with a space group C2/c, which corresponds well with the data of JCPDS 37-1486 card. The crystal structure of ceramic samples kept stable in the sintering temperature range of 875°C–975°C. Homogeneous microstructures with little pores can be observed for the $Zn_3B_2O_6$ ceramic sintered at 925°C for 4 h. The grain sizes of the ceramic were between 1 and 15 μm.

Figure 2 presents the variation of bulk densities as a function of sintering temperature of $Zn_3B_2O_6$ ceramics. As the sintering temperature increases from 875°C to 925°C, the density increases from ~3.52 to 3.68 g/cm^3, which is equivalent to a relative density of about 96% of the theoretical density. When the sintering temperature increases to 950°C, there was almost no change for the density. But a tiny decrease occurred on the curve when the temperature reaches 975°C, which indicates that the ceramic was excessively sintered. This result indicates that the densified temperature of the $Zn_3B_2O_6$ ceramic is ~925°C–950°C.

The dielectric constant and $Q \times f$ values of $Zn_3B_2O_6$ ceramics as a function of the sintering temperature are shown in Fig. 3. As the sintering temperature increases, microwave dielectric constant increases with a trend similar to their density for the density and dielectric constant of ceramic are associated with the elimination of the pores.[18] The maximum dielectric constant was obtained when the samples were sintered at 975°C for 4 h. The $Q \times f$ values of $Zn_3B_2O_6$ ceramics reach a maximum with a value ~58 500 GHz (at 10.97 GHz). Many factors are believed to affect the microwave dielectric loss and these can be divided into two parts: the intrinsic loss and the extrinsic loss. Intrinsic loss is mainly caused by lattice vibration modes whereas extrinsic loss is dominated by second phases, oxygen vacancies, grain sizes, and densification or porosity.[19] The porosity plays an important role in controlling the dielectric losses. When the porosity decreases, the relative densities of the ceramics increase which cause the dielectric losses' decrease, so the $Q \times f$ values of $Zn_3B_2O_6$ ceramics are closely related to their porosity. The τ_f does not change remarkably with increasing sintering temperature and remains stable at about −58 ppm/°C.

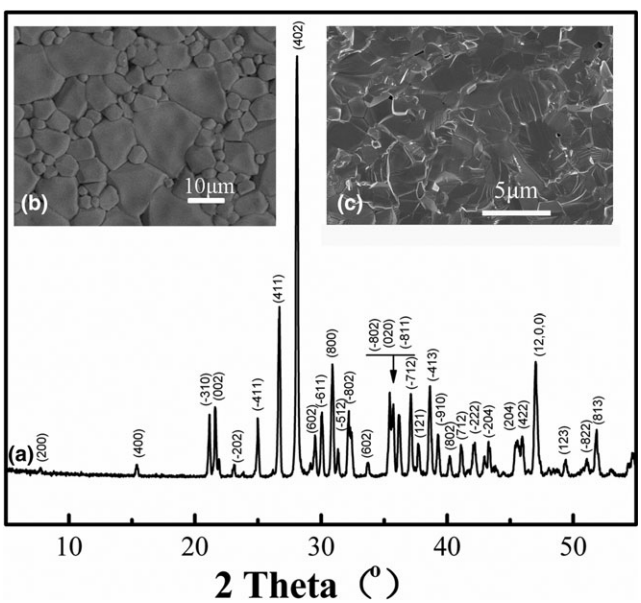

Fig. 1. The XRD result (a), SEM of the surface (b), cross section (c) of $Zn_3B_2O_6$ ceramic sintered at 925°C for 4 h.

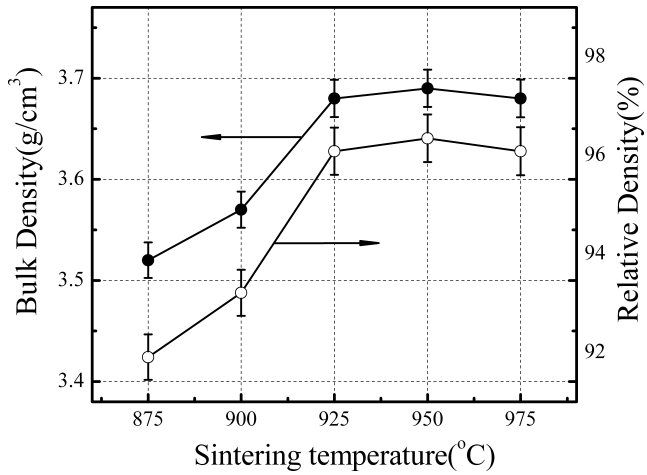

Fig. 2. Bulk densities of $Zn_3B_2O_6$ ceramics as a function of sintering temperatures.

For LTCC application of a new microwave dielectric ceramic, its chemical compatibility with silver electrodes should be studied. Figure 4 shows the BEI micrographs of the as-fired surface, EDS analysis and XRD results of a $Zn_3B_2O_6$ ceramic with 20 wt% Ag addition co-fired at 950°C for 2 h. In XRD patterns, there are only peaks of the $Zn_3B_2O_6$ phase and a pure silver phase. In the BEI photo of the silver co-fired ceramic, it is obvious that there are two kinds of grains: most grains with dark color and small grains with bright color. From EDS analysis, it is identified that the grains with dark color belong to $Zn_3B_2O_6$ phase and the small grains with bright color are found to be pure silver. Combined with the XRD results, it can be concluded that the $Zn_3B_2O_6$ ceramic does not react with silver at 950°C. This makes $Zn_3B_2O_6$ ceramic a promising dielectric material for LTCC substrate application.

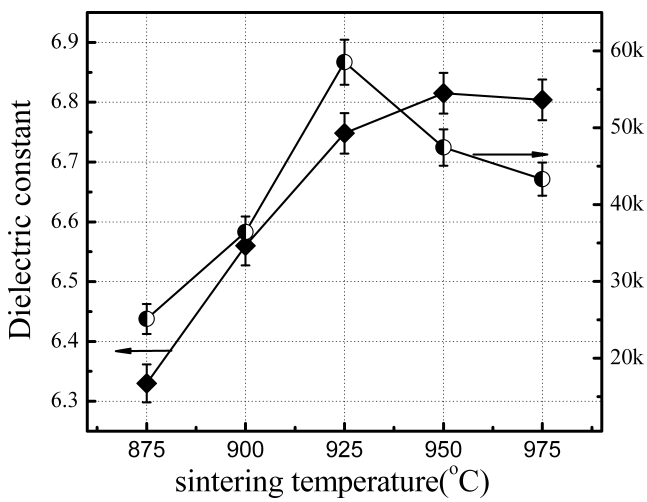

Fig. 3. The dielectric constant and $Q \times f$ values of $Zn_3B_2O_6$ ceramics as a function of sintering temperature.

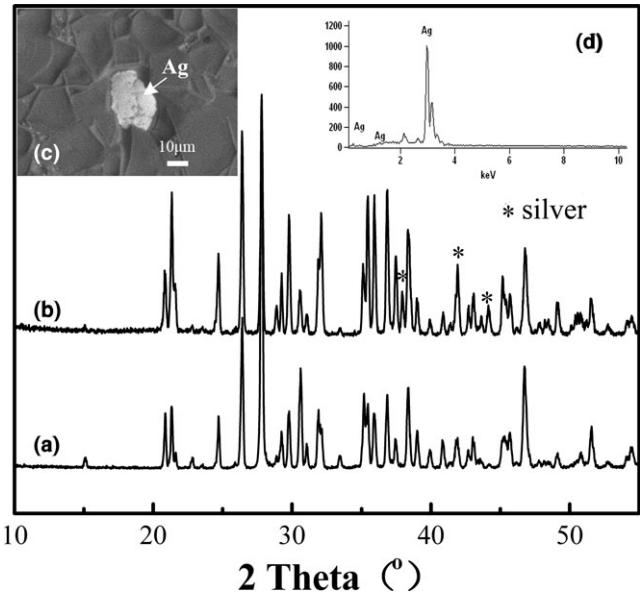

Fig. 4. The XRD result of the $Zn_3B_2O_6$ ceramic sintered at 925°C for 4 h (a) and XRD results (b), Backscattered electron imaging micrographs (c) and EDS analysis (d) of the $Zn_3B_2O_6$ ceramic co-fired with 20 wt% silver (Ag) addition at 950°C for 2 h.

IV. Conclusion

In summary, the $Zn_3B_2O_6$ ceramic was prepared via traditional solid-state reaction methods. High performance of microwave dielectric properties was obtained in the $Zn_3B_2O_6$ ceramics sintered at 925°C with a microwave permittivity of 6.8, a $Q \times f$ value about 58 535 GHz at 10.79 GHz and a temperature coefficient value of −58 ppm/°C. From the XRD, BEI micrographs, and EDS results of the $Zn_3B_2O_6$ powder co-fired with silver electrode, it was found that the $Zn_3B_2O_6$ ceramic is chemically compatible with silver at its sintering temperature. All these results indicate that the $Zn_3B_2O_6$ ceramic is a promising candidate for LTCC substrate application.

Acknowledgments

This work was supported by National 973-project of China (2009CB623302), National Science Foundation of China (61025002, 10979035) and International Science and Technology Collaboration Project of China (2009DFA51820).

References

[1]M. T. Sebastian and H. Jantunen, "Low Loss Dielectric Materials for LTCC Applications: A Review," *Int. Mater. Rev.*, **53**, 57–90 (2008).
[2]R. R. Tummala Rao, "Ceramic and Glass Packaging in the 1990s," *J. Am. Ceram. Soc.*, **74** [5] 895–908 (1991).
[3]P. S. Anjana and M. T. Sebastian, "Microwave Dielectric Properties and Low-Temperature Sintering of Cerium Oxide for Ltcc Applications," *J. Am. Ceram. Soc.*, **92** [1] 96–104 (2009).
[4]J. Guo, D. Zhou, H. Wang, and X. Yao, "Microwave Dielectric Properties of (1−x) $ZnMoO_4$–$XTiO_2$ Composite Ceramics," *J. Alloys Compd.*, **509** [19] 5863–5 (2011).
[5]A. Stiegelschmitt, A. Roosen, C. Ziegler, S. Martius, and L. P. Schmidt, "Dielectric Data of Ceramic Substrates at High Frequencies," *J. Eur. Ceram. Soc.*, **24** [6] 1463–6 (2004).
[6]A. Bittner and U. Schmid, "The Porosification of Fired Ltcc Substrates by Applying a Wet Chemical Etching Procedure," *J. Eur. Ceram. Soc.*, **29** [1] 99–104 (2009).
[7]D. Zhou, W. Wu, H. Wang, Y. S. Jiang, and X. Yao, "The Two Element Antennas Using $BiNbO_4$ Ceramics as the Substrate," *Mater. Sci. Eng., A*, **460** [15] 652–5 (2007).
[8]J. Bang, "Microwave Dielectric Properties of $MgCo_2(VO_4)_2$ Ceramics Synthesized by a Sol-Gel Method," *J. Eur. Ceram. Soc.*, **27** [13–15] 3855–9 (2007).
[9]M. Udovic, M. Valant, and D. Suvorov, "Dielectric Characterization of Ceramics From the TiO_2-TeO_2 System," *J. Eur. Ceram. Soc.*, **21** [10–11] 1735–8 (2001).
[10]M. Udovic, M. Valant, and D. Suvorov, "Phase Formation and Dielectric Characterization of the Bi_2O_3-TeO_2 System Prepared in an Oxygen Atmosphere," *J. Am. Ceram. Soc.*, **87** [4] 591–7 (2004).
[11]N. K. James and R. Ratheesh, "Microwave Dielectric Properties of Low-Temperature Sinterable $BaCe_2(MoO_4)_4$ Ceramics," *J. Am. Ceram. Soc.*, **93** [4] 931–3 (2010).
[12]G. Subodh, R. Ratheesh, M. V. Jacob, and M. T. Sebastian, "Microwave Dielectric Properties and Vibrational Spectroscopic Analysis of $MgTe_2O_5$ Ceramics," *J. Mater. Res.*, **23** [6] 1551–6 (2008).
[13]U. Došler, M. M. Kržmanc, B. Jančar, and D. Suvorov, "A High-Q Microwave Dielectric Material Based on $Mg_3B_2O_6$," *J. Am. Ceram. Soc.*, **93** [11] 3788–92 (2010).
[14]U. Došler, M. M. Kržmanc, and D. Suvorov, "The Synthesis and Microwave Dielectric Properties of $Mg_3B_2O_6$ and $Mg_2B_2O_5$ Ceramics," *J. Eur. Ceram. Soc.*, **30** [2] 413–8 (2010).
[15]D.-G. Chen, W.-D. Cheng, D.-S. Wu, H. Zhang, Y.-C. Zhang, Y.-J. Gong, and Z.-G. Kan, "Syntheses, Band Structures and Optical Properties of $Zn_3B_2O_6$ and $KZn_4B_3O_9$," *Solid State Sci.*, **7** [2] 179–88 (2005).
[16]D. E. Harrison, "Lamellar Glass-Crystal Structures in the System ZnO-B_2O_3," *J. Cryst. Growth*, **3–4**, 674–8 (1968).
[17]J. Krupka, K. Derzakowski, B. Riddle, and J. B. Jarvis, "A Dielectric Resonator for Measurements of Complex Permittivity of low Loss Dielectric Materials as a Function of Temperature," *Meas. Sci. Technol.*, **9** [10] 1751–6 (1998).
[18]M. Valant, D. Suvorov, R. C. Pullar, K. Sarma, and N. M. Alford, "A Mechanism for Low-Temperature Sintering," *J. Eur. Ceram. Soc.*, **26** [5–6] 2777–83 (2006).
[19]S. J. Penn, N. M. Alford, A. Templeton, X. Wang, M. Xu, M. Reece, and K. Schrapel, "Effect of Porosity and Grain Size on the Microwave Dielectric Properties of Sintered Alumina," *J. Am. Ceram. Soc.*, **80** [7] 1885–8 (1997). □