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Journal of the European Ceramic Society 32 (2012) 521–524

www.elsevier.com/locate/jeurceramsoc

Short communication

Preparation and microwave dielectric properties of $3ZnO\cdot B_2O_3$ ceramics with low sintering temperature

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Received 29 June 2011; received in revised form 23 September 2011; accepted 1 October 2011
Available online 22 October 2011

Abstract

The preparation and dielectric properties of $3ZnO\cdot B_2O_3$ ceramics were investigated. Dense $3ZnO\cdot B_2O_3$ ceramics were obtained as sintered in the temperature range from 950 to 1000 °C for 3 h. The X-ray diffraction showed that the obtained ceramics were of a monoclinic $3ZnO\cdot B_2O_3$ structure. The ceramic specimens fired at 955 °C for 1 h exhibited excellent microwave dielectric properties: $\varepsilon_r \sim 6.9$, $Q \times f \sim 20{,}647$ GHz (@6.35 GHz), and $\tau_f \sim -80$ ppm/°C. The dependences of relative density, ε_r, and $Q \times f$ of ceramics sintered at 955 °C on sintering soaking time showed that they all reached their plateaus as the soaking time was up to 60 min. Meanwhile, $3ZnO\cdot B_2O_3$ ceramics had no reaction with silver during cofiring, indicating it is a potential candidate for low-temperature cofired ceramic (LTCC) substrate.

Keywords: Sintering; Microstructure-final; Dielectric properties; $3ZnO\cdot B_2O_3$; Substrates

1. Introduction

With the rapid growth of mobile and wireless telecommunication system in the consumer electronic market, the low-temperature cofired ceramic (LTCC) technology is playing an important role in the development of various electronic modules and substrates. By the LTCC technology, ceramic dielectrics and low-melting metallic conductors are stacked and cofired in multilayers in special patterns to fulfill different electrical functions. Generally ceramic dielectrics are required to have a low sintering temperature (<950 °C) and a low relative permittivity (usually $\varepsilon_r \sim 4$–9).[1]

Recently, compound ceramic systems with originally low sintering temperature have been investigated for LTCC application without addition of any sintering aids. These systems include binary systems AO–TeO_2 (A = Ba, Ca),[2–5] JO–WO_3 (J = Mg, $Li_{1/2}Bi_{1/2}$),[6,7] MgO–V_2O_5,[8] and RO–MoO_3 (R = Mg, Ba, Mn),[9] and $Bi_{12}MO_{20-\delta}$ (M = Si, Ge, Ti, Pb, Mn or $B_{1/2}P_{1/2}$).[10] However, among these systems, AO–TeO_2 and $LiBiW_2O_8$ ceramics seem to react with Ag electrode,[2–5,7] MgO–V_2O_5 ceramics needs long sintering soaking time,[8] and $Bi_{12}MO_{20-\delta}$ ceramics exhibits relatively low quality factor ($Q \times f$) (∼8000 GHz).[10] These drawbacks limit their further application in LTCC. So there is always much interest in searching for new ceramic systems with much better sintering and microwave dielectric properties.

In the ZnO–B_2O_3 binary system, at least three zinc borate phases exist and the temperature dependence of their stability was reported very early.[11] Recently different zinc borate single crystals were synthesized as potential optical compounds,[12–14] and zinc borate glass was used as sintering aid in other ceramics to lower their sintering temperatures due to its low softening point.[15–17] However no papers reported the preparation and microwave dielectric properties of zinc borate dense ceramics. In this present paper, we report the low-temperature preparation of ceramics of $3ZnO\cdot B_2O_3$ (also described as a phase with the composition $5ZnO\cdot 2B_2O_3$[18,19]), without addition of any sintering aids, by the traditional ceramic process. This simple ceramic system shows originally low sintering temperature and excellent microwave dielectric properties.

2. Experimental

The materials were prepared by the conventional solid state ceramic oxide route. Starting chemicals of ZnO (>99.9%,

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doi:10.1016/j.jeurceramsoc.2011.10.013

Guo-Yao Co. Ltd., Shanghai, China), H_3BO_3 (>99.9%, Guo-Yao Co. Ltd., Shanghai, China) were weighed in a nominal composition of $5ZnO\cdot 2B_2O_3$, dry mixed thoroughly, and calcined at 750 °C for 1 h. Then the calcined powder was ball milled with de-ionized water using zirconia balls for 3 h, and dried. For homogeneity, the dried powder was calcined at 750 °C for 1 h, wet ball milled, and dried again. The dried powder was pelletized with 8 wt% PVA binder and bilaterally pressed into cylindrical compacts of 25 mm in diameter and about 20 mm in height under a pressure of 100 MPa. The green specimens were fired in a temperature range from 930 to 1000 °C for 3 h. In addition, the effect of sintering time was investigated by firing the green specimens at 955 °C for different soaking times of 15 min to 2 h. The sample for the test of cofiring compatibility with Ag was prepared by mixing the calcined powder with 50 wt% of $AgNO_3$ powder.

Crystalline phases of the sintered samples were identified with an X-ray diffractometer (Rigaku D/MAX-RB, Tokyo, Japan) using a Cu Kα target within 2θ range of between 10° and 80°. The bulk densities of sintered specimens were measured by the Archimedes method. The microstructures of sintered compacts were observed from fracture surfaces by scanning electron microscopy (SEM, Sirion 200, FEI, Netherlands).

The ε_r and $Q\times f$ values were determined using a silver coated cavity ca. 4 times the diameter of the test resonator (this ensured an isolated but shielded resonator) and an Agilent network analyzer (E5071 C) operating in the $TE_{01\delta}$ resonance mode in reflectance.[20,21] For the measurement of the temperature coefficient of resonant frequency (τ_f), the technique is the same as that of $Q\times f$ measurement. The test cavity was placed over a thermostat and the temperature range used was from 30 to 80 °C. The τ_f values were calculated as follows:

$$\tau_f = \frac{f_{80}-f_{30}}{f_{30}(80-30)} \tag{1}$$

where f_{80} and f_{30} are the resonant frequencies at 80 and 30 °C, respectively.

3. Results and discussion

Fig. 1a–d shows the room temperature X-ray diffraction (XRD) patterns of $3ZnO\cdot B_2O_3$ ceramics sintered at different temperatures in the range from 930 to 1000 °C for 3 h. The XRD patterns of $3ZnO\cdot B_2O_3$ ceramics sintered at these temperatures are considered to attribute to a single phase which corresponds to the $3ZnO\cdot B_2O_3$ (JCPDS 71–2063) with a monoclinic structure under the detection limit of the instrument, and the crystal structure of ceramic samples did not change with the increasing temperature. The XRD pattern of $3ZnO\cdot B_2O_3$ ceramic cofired with Ag in the Fig. 1e shows no evidence of the formation of secondary phase except silver, indicating that the $3ZnO\cdot B_2O_3$ ceramic has a chemical compatibility with silver during cofiring.

The microstructure evolution of $3ZnO\cdot B_2O_3$ ceramics was investigated as a function of sintering temperature. Fig. 2 shows the SEM images of the fracture surfaces of ceramic samples sintered at different temperature for 3 h. The sample sintered at 930 °C was obviously porous with irregular shape pores and small grains of about 5 μm in size, indicating its insufficient sintering (Fig. 2a). As the sintering temperature was up to 950 °C, the ceramic turned much denser and less small pores with irregular shape were left (Fig. 2b). At 975 °C grains grew greatly, and few large spherical pores formed (Fig. 2c). These spherical pores originated from the gas inside the ceramics.[22] When the sintering temperature reached up to 1000 °C, the number of the spherical pores in ceramics increased (Fig. 2d), indicating that the sample was excessively sintered.[22]

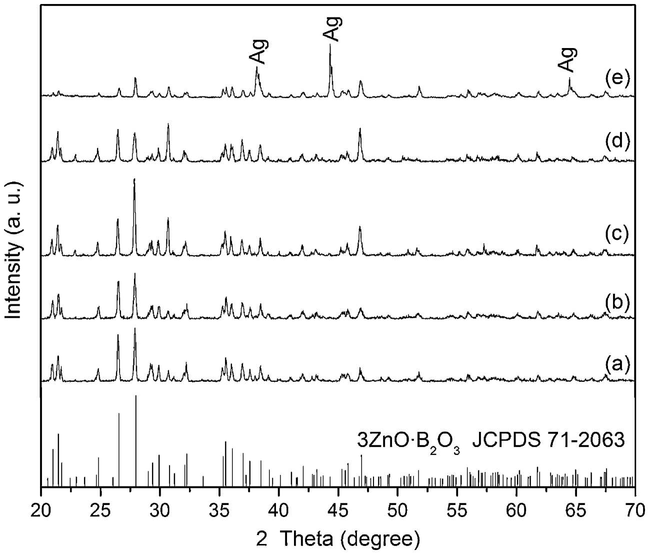

Fig. 1. XRD patterns of $3ZnO\cdot B_2O_3$ ceramics (a)–(d) sintered at 930 °C, 950 °C, 975 °C, and 1000 °C, respectively, for 3 h, and (e) cofired with silver at 955 °C for 30 min.

Fig. 3 shows the bulk density and microwave dielectric properties of $3ZnO\cdot B_2O_3$ ceramics sintered at various sintering temperatures for 3 h. The ceramics fired at 930 °C had a bulk density of about 2.88 g/cm^3 (68% of TD) with a relatively low shrinkage of 15.2%, implying that it was not dense. As fired at 950 °C the ceramics reached the maximum in density of 4.07 g/cm^3 (96% of TD) with a shrinkage of 23.9%. With further increase in firing temperature the density of ceramics slightly decreased. The bulk density results were in good agreement with the SEM observation. The dependence of ε_r of $3ZnO\cdot B_2O_3$ ceramics on sintering temperature had a tendency similar to that of the bulk density. As the firing temperature was up to 950 °C, ε_r reached a maximum of 6.9. However, $Q\times f$ value of $3ZnO\cdot B_2O_3$ ceramics achieved the maximum of 36,800 GHz (at 6.62 GHz) at 975 °C. With further increase in firing temperature to 1000 °C, the $Q\times f$ value of ceramics decreased substantially to 10,698 GHz (at 6.81 GHz), which might result from the formation of excess glass phase and spherical pores in ceramics. The τ_f value of $3ZnO\cdot B_2O_3$ ceramics ranged from −66 to −114 ppm/°C when the sintering temperature ranged from 930 to 1000 °C.

Fig. 4 shows bulk density, ε_r, and $Q\times f$ value of the $3ZnO\cdot B_2O_3$ ceramics sintered at 955 °C as a function of soaking time in a range from 15 min to 2 h. The bulk density of ceramics increased with the increasing soaking time and reached its plateau value of 4.07 g/cm^3 (96% of TD) at 60 min. The

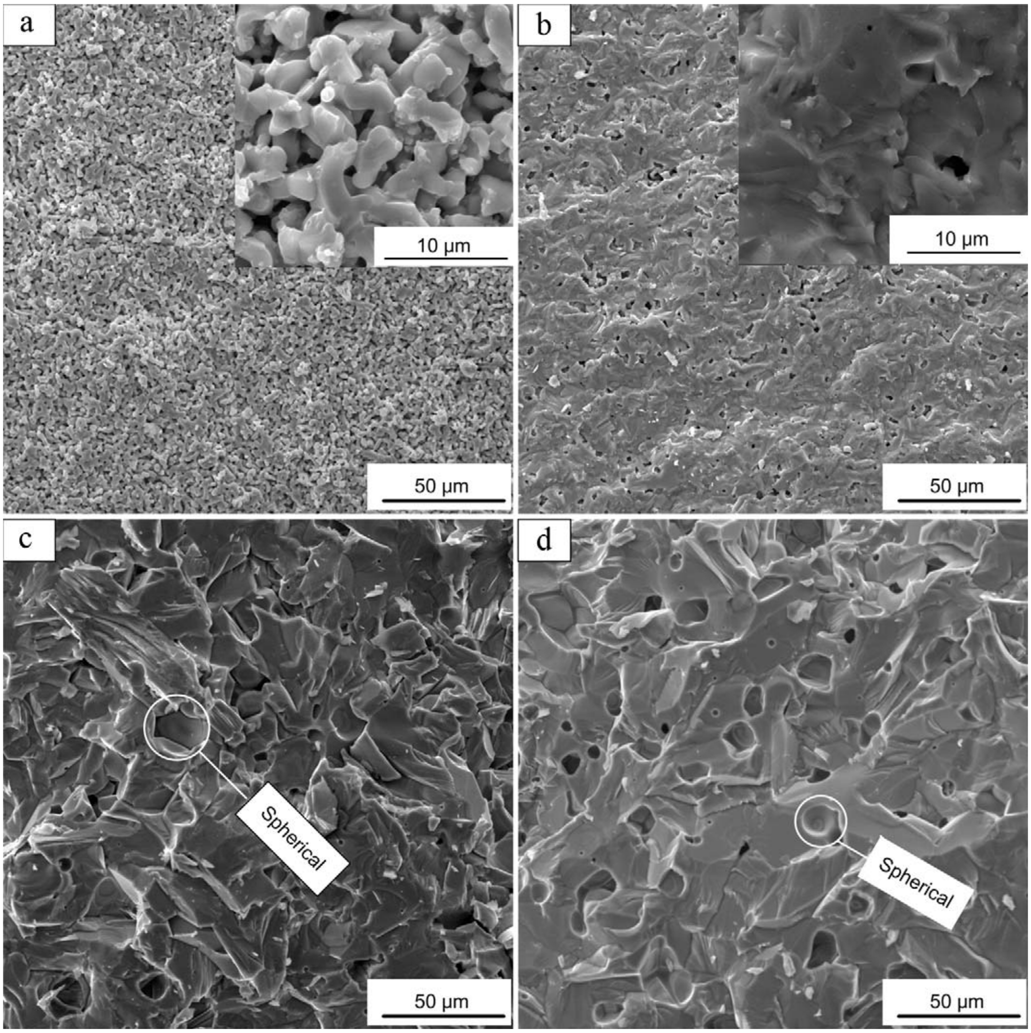

Fig. 2. SEM photographs of $3ZnO{\cdot}B_2O_3$ ceramic samples sintered for 3 h at different temperatures: (a) 930 °C, (b) 950 °C, (c) 975 °C, and (d) 1000 °C.

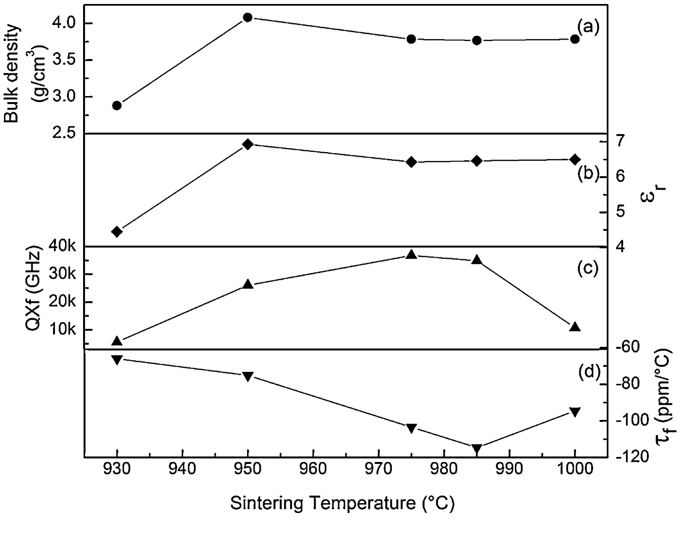

Fig. 3. Bulk density and microwave dielectric properties of $3ZnO{\cdot}B_2O_3$ ceramics sintered at different temperatures for 3 h.

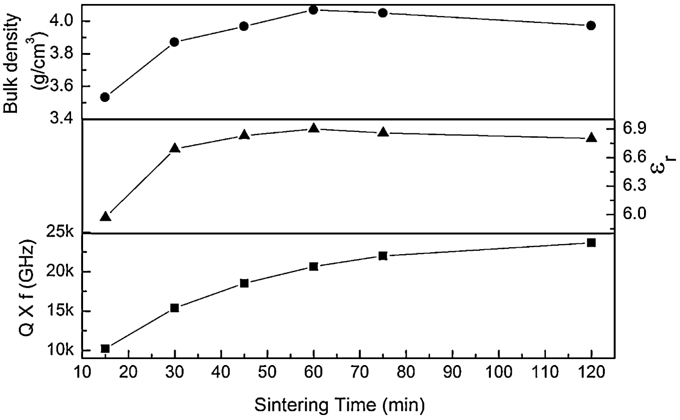

Fig. 4. Bulk density, ε_r, $Q \times f$ of $3ZnO{\cdot}B_2O_3$ ceramics sintered at 955 °C as a function of the soaking time.

dependences of ε_r and $Q \times f$ value of $3ZnO{\cdot}B_2O_3$ ceramics on soaking time had a trend similar to that of the bulk density. The ceramic samples obtained at 955 °C for 60 min exhibited an ε_r and $Q \times f$ value of 6.9 and 20,647 GHz (at 6.35 GHz) respectively. These results suggest that sintering at 955 °C for 60 min is sufficient for the densification of $3ZnO{\cdot}B_2O_3$ ceramics.

Based on the above-mentioned XRD, SEM, density, and dielectric property results (Figs. 1–4), it is concluded that the optimal sintering temperature of $3ZnO{\cdot}B_2O_3$ ceramics approximately ranges from 950 to 985 °C. Samples sintered at these temperatures were dense and of excellent dielectric properties. All these optimal sintering temperatures were below the melting point (1080 °C) of $3ZnO{\cdot}B_2O_3$ phase as given by the phase diagram from Leonov.[23] Moreover the lower limit of this optimal sintering temperature range was close to the eutectic point (957 °C) in the phase diagram.[23] This implied that a liquid (glass) phase might begin to form and to facilitate the densification of ceramics at this temperature.

4. Conclusion

In the present paper, the preparation and microwave dielectric properties of $3ZnO{\cdot}B_2O_3$ ceramics were studied. $3ZnO{\cdot}B_2O_3$ ceramics can be prepared by the conventional solid state oxide route and well densified at 955 °C for 1 h with a bulk density of 4.07 g/cm^3, which exhibits excellent microwave dielectric properties: $\varepsilon_r = 6.9$, $Q \times f = 20{,}647$ GHz (at 6.35 GHz), and $\tau_f = -80$ ppm/°C. In addition $3ZnO{\cdot}B_2O_3$ ceramics has a chemical compatibility with Ag during cofiring. This simple ceramic system is a potential candidate for LTCC substrate.

Acknowledgements

The authors thank the Analytical and Testing Center, Huazhong University of Science and Technology for XRD and SEM measurements.

References

1. Sebastian MT, Jantunen H. Low loss dielectric materials for LTCC applications: a review. *Int Mater Rev* 2008;**53**(2):57–90.
2. Udovic M, Valant M, Suvorov D. Dielectric characterization of ceramics from the TiO_2–TeO_2 system. *J Eur Ceram Soc* 2001;**21**: 1735–8.
3. Valant M, Suvorov D. Glass-free low-temperature cofired ceramics: calcium germanates, silicates and tellurates. *J Eur Ceram Soc* 2004;**24**:1715–9.
4. Kwon DK, Lanagan MT, Shrout TR. Microwave dielectric properties and low-temperature cofiring of $BaTe_4O_9$ with aluminum metal electrode. *J Am Ceram Soc* 2005;**88**:3419–22.
5. Udovic M, Valant M, Suvorov D. Phase formation and dielectric characterization of the Bi_2O_3–TeO_2 system prepared in an oxygen atmosphere. *J Am Ceram Soc* 2004;**87**:591–7.
6. Pullar RC, Farrah S, Alford NM. $MgWO_4$, $ZnWO_4$, $NiWO_4$ and $CoWO_4$ microwave dielectric ceramics. *J Eur Ceram Soc* 2007;**27**:1059–63.
7. Zhou HF, Chen XL, Fang L, Liu XB, Wang YL. Microwave dielectric properties of $LiBiW_2O_8$ ceramics with low sintering temperature. *J Am Ceram Soc* 2010;**93**(12):3976–9.
8. Umemuraa R, Ogawa H, Ohsato H, Kana A, Yokoi A. Microwave dielectric properties of low-temperature sintered $Mg_3(VO_4)_2$ ceramic. *J Eur Ceram Soc* 2005;**25**:2865–70.
9. Choi GK, Kim JR, Yoon SH, Hong KS. Microwave dielectric properties of scheelite (A = Ca, Sr, Ba) and wolframite (A = Mg, Zn, Mn) $AMoO_4$ compounds. *J Eur Ceram Soc* 2007;**27**:3063–7.
10. Valant M, Suvorov D. Processing and dielectric properties of sillenite compounds $Bi_{12}MO_{20\text{-}(}$(M = Si, Ge, Ti, Pb, Mn, $B_{1/2}P_{1/2}$). *J Am Ceram Soc* 2001;**84**:2900–4.
11. Whitaker A. Temperature dependence of the stability of zinc borates. *J Mater Sci* 1972;**7**:189–93.
12. Chen XA, Xue HP, Chang XA, Zhang L, Zhao YH, Zuo JL, Zang HG, Xiao WQ. Syntheses and crystal structures of the α- and β- forms of zinc orthoborate, $Zn_3B_2O_6$. *J Alloys Compd* 2006;**425**:96–100.
13. Huppertz H, Heymann G. Multianvil high-pressure/high-temperature preparation, crystal structure, and properties of the new oxoborate β-ZnB_4O_7. *Solid State Sci* 2003;**5**:281–9.
14. Harrison WTA, Gier TE, Stucky GD. The synthesis and ab initio structure determination of $Zn_4O(BO_3)_2$, a microporous, zincoborate constructed of fused subunits, of three- and five-membered rings. *Angew Chem Int Ed* 1993;**32**:724–6.
15. Minaev VS, Petrova VZ, Timoshenkov SP, Khafizov RR, Sharagov VA. Glass formation and glass-forming ability of melts in $A^{II}O$–B_2O_3 binary systems ($A^{II}O$ = BeO, MgO, CaO, SrO, BaO, ZnO, CdO). *Glass Phys Chem* 2004;**30**:215–25.
16. Lee YC, Lee WH, Shieu FS. Microwave dielectric properties and microstructures of $Ba_2Ti_9O_{20}$-based ceramics with 3ZnO–B_2O_3 addition. *J Eur Ceram Soc* 2005;**25**:3459–68.
17. Kim JR, Kim DW, Jung HS, Hong KS. Low-temperature sintering and microwave dielectric properties of $Ba_5Nb_4O_{15}$ with ZnB_2O_4 glass. *J Eur Ceram Soc* 2006;**26**:2105–9.
18. Garcia-Blanco S, Fayos J. The crystal structure of zinc orthoborate, $Zn_3(BO_3)_2$. *Z Kristallogr* 1968;**127**:145–59.
19. Eidem MA, Orton BR, Whitaker A. Phase equilibria in the system ZnO–B_2O_3–SiO_2 at 950 °C. *J Mater Sci* 1987;**22**:4139–43.
20. Hakki BW, Coleman PD. A dielectric resonator method of measuring inductive capacities in the millimeter range. *IEEE Trans Micro Theory Tech* 1960;**8**(4):402–10.
21. Courtney WE. Analysis and evaluation of a method of measuring complex permittivity and permeability of microwave insulators. *IEEE Trans Micro Theory Tech* 1970;**18**(8):476–85.
22. Imanaka Y. *Multilayered low temperature cofired ceramics (LTCC) technology*. New York: Springer Science+Business Media Inc; 2005.
23. Levin EM, Robbins CR, McMurdie HF. *Phase diagrams for ceramists*. 2nd Ed. Columbus, Ohio: The American Ceramic Society; 1969. Fig. 301, p. 119.