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Feature article

High quality microwave dielectric ceramic sintered at extreme-low temperature below 200° and co-firing with base metal

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ABSTRACT

Ultra-low temperature co-fired ceramics technology (ULTCC) requires the microwave dielectric ceramics with lower intrinsic sintering temperature than the melting point of inner electrodes. In the present work, a novel HBO_2 ceramic was found to be densified at extreme-low temperature below 200 °C, with pores, residual H_3BO_3, amorphous B_2O_3 inside, with a relative permittivity ~2.12 ± 0.02, a Qf value ~32,700 ± 300 GHz and a temperature coefficient of resonant frequency value ~ − 43 ± 3 ppm/°C. This material can be easily obtained by dehydration from H_3BO_3 by sintering at low temperature below 200 °C. Its extreme-low sintering temperature and water solubility also provides the possibility to achieve some novel multi-functional inorganic-organic composite in the future.

1. Introduction

Microwave dielectric materials have been studied for more than half century and they are widely used in microwave devices as dielectric resonators (DR), filters, capacitors, substrates, etc [1–3]. For traditional microwave dielectric materials, there are three important basic physical parameters: dielectric relative permittivity (ε_r), quality factor $Q \times f$ value ($Q \times f$, where $Q = 1/\text{dielectric loss}$ and f = resonant frequency) and temperature coefficient of resonant frequency (TCF or $\tau_f \approx -\alpha_l - 0.5\tau_\varepsilon$, where α_l is the linear thermal expansion coefficient and τ_ε is the temperature coefficient of relative permittivity) [2–5]. The electromagnetic wavelength and size of the device are inversely proportional to the dielectric relative permittivity. The – 3 dB bandwidth of resonant frequency is inverse proportion to sample's $Q \times f$ value, which means that $Q \times f$ value represents the selectivity in a certain frequency range. TCF determines the temperature dependence of resonant frequency. To meet the requirements of miniaturization and integrations of modern microwave devices needed in fast developed wireless and satellite communication technologies, low temperature co-fired ceramics (LTCC) technology has played an important role in fabrication procedure [1–5]. To lower the sintering temperatures (S.T.) of traditional microwave dielectric ceramics to meet the requirement of LTCC technology, addition of low melting point oxides/fluoride, B_2O_3, V_2O_5, Bi_2O_3, LiF etc., or low softening point glasses, B_2O_3-ZnO, B_2O_3-ZnO-SiO_2 etc., becomes the most popular method [6–9]. Usually traditional multilayer co-fired ceramics (MLCC) technology employs high temperature firing ceramics and uses noble metals (Pt, Pd, Pd-Ag) as inner electrodes. LTCC technology enables base metals, such as Ag, Ni, Cu, etc., to be employed in multi-layer co-fired devices with low firing electroceramics.

Recently, due to research on microwave dielectric ceramics with low intrinsic sintering temperature, the so-called ultra-low temperature co-fired ceramics (ULTCC) technology has attracted much attention. The two classic examples are $BaTe_4O_9$ (ε_r = 17.5, Qf = 54,700 GHz and sintering temperature S.T. = 550 °C) and $Bi_2Mo_2O_9$ (ε_r = 38, Qf = 12,500 GHz and S. T. = 620 °C) ceramics [10,11]. Both of them are chemically compatible with aluminum, which means that Al can be used as the inner electrode and it is much cheaper than the mostly used silver. As summarized in our previous work [12], there might be novel ULTCCs with constituents with low-melting-point oxides, such as TeO_2 (733 °C), MoO_3 (795 °C), Bi_2O_3 (817 °C), PbO (886 °C), B_2O_3 (450 °C) or H_3BO_3 (171 °C), P_2O_5 (340 °C), V_2O_5 (690 °C), Li_2CO_3 (723 °C), etc. In our previous work [4,11–16], a series of novel ultra-low temperature firing microwave dielectric ceramic materials, including low relative permittivity (<20), medium relative permittivity (20–45) and high relative permittivity (>45) dielectrics, have been explored in the Bi_2O_3-MoO_3 binary system, Li_2O-Bi_2O_3-MoO_3

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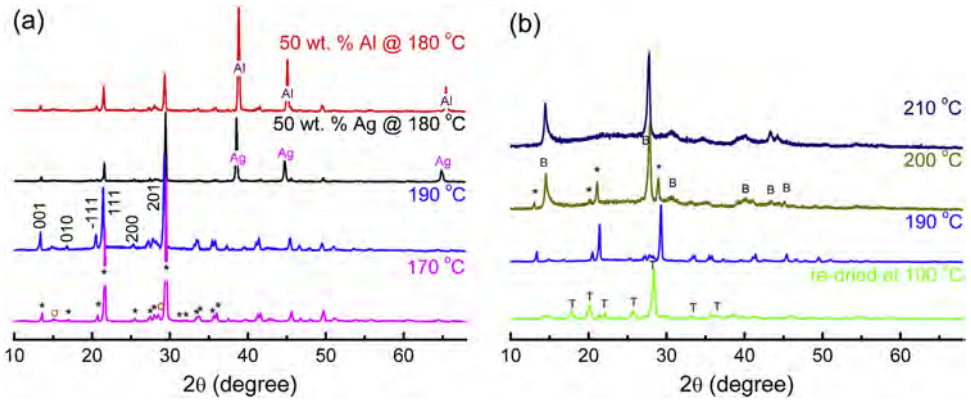

Fig. 1. XRD patterns of ceramic samples sintered at 170 °C, 190 °C, and co-fired samples with 40 wt.% Al and Ag powders at 180 °C (a) (*—HBO_2, o—H_3BO_3), sintered at 200 °C, 210 °C, and dried sample (at 100 °C) after being dissolved in water (b) (T—HBO_2-III, B—B_2O_3).

ternary system and Li_2O-Bi_2O_3-MoO_3-V_2O_5, Na_2O-Bi_2O_3-MoO_3-V_2O_5, Fe_2O_3-Bi_2O_3-MoO_3-V_2O_5 quaternary systems etc. In our recent work [17], a novel spinel structured $NaAgMoO_4$ was reported to be well densified at 400 °C with a relative permittivity ~7.9, a Qf value ~33,000 GHz and a TCF ~120 ppm/°C. It possesses the lowest sintering temperature among all the reported microwave dielectric materials prepared by using traditional solid state reaction method. Study on ULTCC technology requires microwave dielectric ceramics to be as "cold" as organic materials. Application of aluminum and silver ink electrodes, which are chemically compatible with ULTCCs, makes it possible to fabricate novel flexible and multi-functional structures for electric devices. Here we can speculate that more microwave dielectric materials with ultra-low processing temperature will be explored not only in low melting point oxides, but also in sulfide, iodide and even coordination complex. Recently, a so-called cold sintering method was proposed and many water soluble microwave dielectric ceramics can be prepared by using this method to achieve a high relative density by a re-crystallization in oversaturated solutions [18–24]. In the present work, we report the processing, sintering behavior and microwave dielectric properties of novel HBO_2 ceramics sintered below 200 °C.

2. Experimental procedure

Reagent-grade H_3BO_3 (>99%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, People's Republic of China) was used as initial material. Powders were pressed into cylinder samples with dimension 15 mm (diameter) *7 mm (height) at 25 MPa without any binder addition. Samples were sintered at temperatures from 172 °C to 190 °C for 2 h. Room temperature X-ray diffraction (XRD) was performed by using a XRD with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). Diffraction pattern was obtained between 2θ of 10–70° at a step size of 0.02°. As-fired surfaces were observed by using a scanning electron microscopy (SEM, FEI, Quanta 250 F). Microwave dielectric properties were measured using the $TE_{01\delta}$ dielectric resonator method with a network analyzer (HP 8720 Network Analyzer, Hewlett-Packard) and a temperature chamber (Delta 9023, Delta Design, Poway, CA). The temperature coefficient of resonant frequency TCF (τ_f) was calculated with the following formula:

$$TCF(\tau_f) = \frac{f_T - f_{T_0}}{f_{T_0} \times (T - T_0)} \times 10^6, \quad (1)$$

where f_T and f_{T0} are the $TE_{01\delta}$ resonant frequencies at temperature T and T_0, respectively.

3. Results and discussion

XRD patterns of ceramic samples sintered at 170 °C, 190 °C, and co-fired samples with 40 wt.% Al and Ag powders at 180 °C are shown in Fig. 1(a). It can be seen that almost pure HBO_2 was obtained after being sintered above 170 °C due to the dehydration of H_3BO_3. When sintering temperature increased to 190 °C, there was still weak trace of H_3BO_3 phase observed and this might be caused by the cladding effect of HBO_2 on the surface of H_3BO_3. In fact, as reported in the literature, there are three modifications of HBO_2 with different melting points: orthorhombic HBO_2-III (~176 °C), monoclinic HBO_2-II (~200.9 °C) and cubic HBO_2-I (236 °C) [25,26]. In the present work, only monoclinic HBO_2-II was observed in ceramic samples. As shown in Fig. 1(b), when sintering temperature reaches 200 °C, the HBO_2 partially decomposed to B_2O_3 phase, along with a wide peak between 20 and 30° which is corresponding to amorphous phase. When sintering temperature reached 210 °C, no peaks of HBO_2 could be detected, which means that the decomposing is complete. To study its chemical compatibility with base metals, 40 wt.% Al and Ag powders were mixed with H_3BO_3, respectively, and co-fired at 180 °C for 2 h. As expected, there were no obvious secondary phases revealed besides HBO_2 and metals. As known to our knowledge, there are no B-Ag-O or B-Al-O compounds formed at such low sintering temperature. Furthermore, it is necessary to study interface and shrinkage match between HBO_2 ceramic and metal paste in multilayer samples. During the whole processing, no water was employed for preparation of HBO_2 ceramic. To test the stability of HBO_2 (HBO_2-II) in water, one sample (sintered at 190 °C) was put into a chamber with high moisture atmosphere and another one is dissolved in water. After drying at 100 °C, both samples took on an orthorhombic structure (HBO_2-III) as shown in Fig. 1(b), which means that dissolution in water can induce the phase transition between different modifications of HBO_2.

Differential scanning calorimetry (DSC) and thermogravimetry (TG) analysis of H_3BO_3 powders in the temperature range 25 ~ 300 °C is shown in Fig. 2. As seen from the DSC curve, there are two endothermic peaks at 139 °C and 163 °C, respectively, which correspond to decomposition of H_3BO_3 into H_2O and HBO_2. Consequently, remarkable weight loss was observed from the TG curve and the weight loss amount further confirms dehydration of the H_3BO_3.

SEM images of pure HBO_2 ceramic sintered at different temperatures, back scattered electron image of co-fired samples with Ag and Al powders at 180 °C and the optical photos of ceramics are shown in Fig. 3. It can be seen from Fig. 3(a), dense microstructure can be observed in HBO_2 ceramic sintered at 180 °C and its grain

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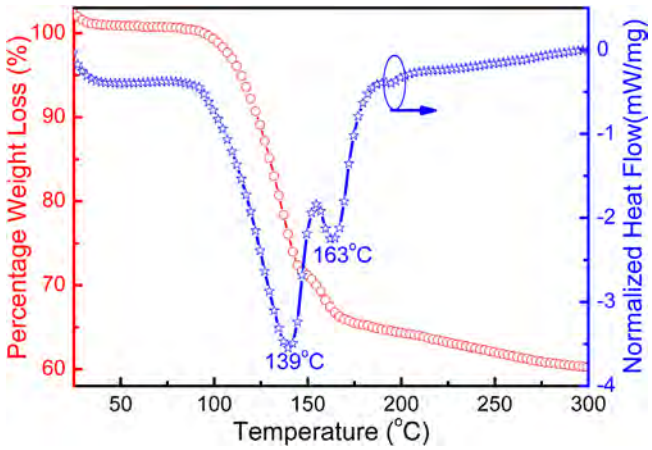

Fig. 2. Differential scanning calorimetry (DSC, normalized heat flow) and thermogravimetry (TG, percentage weight loss) analysis of H_3BO_3 powders in the temperature range 25–300 °C.

size lied between 3 and 10 μm. In co-fired ceramic samples as seen from Fig. 3(b) and (c), both the grain of metal and HBO_2 phases can be clearly observed, which further confirms the chemical compatibility between them. All the HBO_2 ceramic took on a white color as shown in Fig. 3(d). Although HBO_2 ceramic might absorb a little water in the air, the cylinder sample was strong enough and can not be broken by hand. Besides, it was also difficult to be smashed by metal tools. As shown in Fig. 3(d), HBO_2 started to partially melt when sintering temperature is above 190 °C. When sintering temperature increased to about 215 °C, some transparent parts inside sample could be observed. The transparent parts became more and more with the increase of sintering temperature and incubation time. The whole sample is almost transparent after being sintered at 220 °C for 4 h as shown in Fig. 3(d). In fact, the transparent materials are a mixture of crystallized B_2O_3 and amorphous B_2O_3 as analyzed as following by XRD technique. When sintering temperature is higher, the sample melted completely. As discussed above, pure HBO_2 can be dissolved in water quickly (in s). When sintering temperature is above 200 °C, the crystallized and amorphous B_2O_3 were detected in samples as seen from XRD analysis. As know to all, B_2O_3 is only a little soluble in water (room temperature). After being placed inside liquids for 24 h at room temperature, it was found that sample sintered at 200 °C can not be dissolved both in water and ethanol, which corresponds well with the existence of B_2O_3 phase.

HBO_2 is easy to be dissolved in water but only a little soluble in acetone. Hence, acetone was chosen as liquid to measure the bulk density of HBO_2 ceramics by using Archimedes' method. The bulk densities of HBO_2 ceramics as a function of sintering temperature are presented in Fig. 3(e) and the saturated value is about $1.429 \pm 0.003\ g/cm^3$. The theoretical density of monoclinic HBO_2 is about $2.04\ g/cm^3$ and the relative density is only about 70.3% not that high as expected. It is not easy to give a simple explanation. There should be pores, residual H_3BO_3 ($1.56\ g/cm^3$), amorphous B_2O_3 inside the HBO_2 ceramic. Existence of any of them will decrease the density seriously. In our future work, some novel processing methods will be employed to achieve single phase HBO_2 ceramics.

Microwave dielectric relative permittivity, Qf value and TCF values of HBO_2 ceramics sintered at 172–186 °C at resonant frequency 14.7–15 GHz are shown in Fig. 4. It is seen that its dielectric relative permittivity reached about 2.19 ± 0.02 when sintering temperature is above 174 °C and kept stable up to 180 °C. When sintering temperature increased further, relative permittivity slightly decreased to 2.12 ± 0.02 at 186 °C, which might be attributed to partial melting. Such a small relative permittivity can be explained by the small ionic polarizability of B^{3+} ($0.05\ Å^3$), which is the smallest one among all the ions in periodic table as predicted by Shannon (besides H^+) [27]. At microwave region, the polarizability is the sum of both ionic and electronic components. Shannon[27] suggested that molecular polarizabilities of complex substances could be estimated by

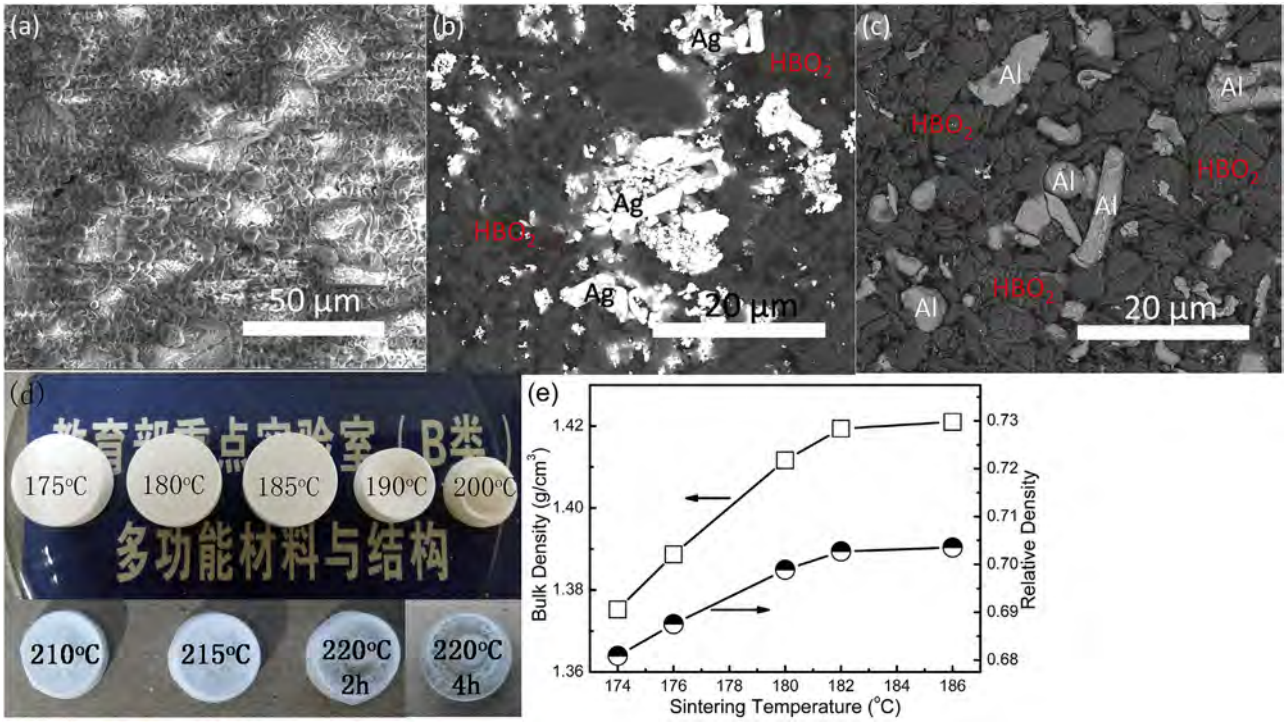

Fig. 3. SEM images of pure HBO_2 ceramic sintered at 180 °C (a), back scattered electron images of co-fired samples with Ag (b), Al (c), powders at 180 °C, optical images of samples sintered at different temperatures (d), and bulk density as a function of sintering temperature (e).

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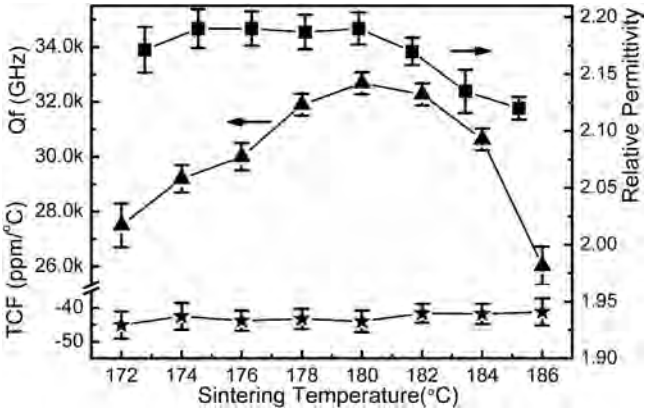

Fig. 4. Microwave dielectric relative permittivity, Qf value and TCF values of HBO_2 ceramics sintered at 172–186 °C at resonant frequency 14.7–15 GHz.

summing the polarizabilities of constituent ions. Then the polarizabilities α could be obtained as follows:

$$\alpha_{HBO_2} = \alpha_{H^+} + \alpha_{B^{3+}} + 2\alpha_{O^{2-}} \approx 0.05 + 4.02 = 4.07\text{Å}^3, \quad (2)$$

The ionic polarization of B^{3+} and O^{2-} 0.05 Å^3 and 2.01 Å^3, respectively. Due to the small ionic size of H^+, its polarization was ignored here. Considering the Clausius–Mosotti relation as follow:

$$\varepsilon = \frac{3V + 8\pi\alpha}{3V - 4\pi\alpha}, \quad (3)$$

where the V is the cell volume, 425.7/12 = 35.475 Å^3. The calculated dielectric relative permittivity is about 3.78, which is a larger than the measured value 2.12. As discussed above, there should be pores, residual H_3BO_3 (1.56 g/cm^3), amorphous B_2O_3 inside the HBO_2 ceramic. If there are only pores and HBO_2 in the sample, the influence of pores on the relative permittivity can be compensated by Bosman and Havinga's correction:[28,29]

$$\varepsilon_r = \varepsilon_{meas} \times (1 + 1.5P), \quad (4)$$

where P is porosity. The compensated relative permittivity is about 3.074, which is still smaller than that calculated from Shannon's additive rule, which can reversely derive that besides pores there should be other secondary phases. Although the relative permittivity of H_3BO_3 and amorphous B_2O_3 is still unknown, they should be larger than that of pores (≈1). Anyway, the difference between measured and calculated relative permittivity values could be explained by the co-existence of residual H_3BO_3 and amorphous B_2O_3 inside the HBO_2 ceramics as discussed above. Compared with the microwave dielectric database summarized by Sebastian recently [5], it is smaller than that of $AlPO_4$ + 5 wt.% MgF_2 ceramic (ε_r = 3.0 and Qf = 900 GHz) sintered at 1450 °C and the traditional SiO_2 sintered 1100 °C at (ε_r = 3.7 and Qf = 44,300 GHz) [30,31]. Qf values of HBO_2 ceramic increased almost linearly from 27,500 ± 400 GHz to 32,700 ± 300 GHz as sintering temperature increased from 172 °C to 180 °C and then decreased sharply with further increase of sintering temperature. The up-limit of Qf value is determined by phonon absorption strongly related to crystal structure. However, the real Qf value is quite sensitive to the sintering process because of extrinsic dielectric loss at microwave regions introduced by defects in ceramics. TCF values kept stable at about −43 ± 3 ppm/°C and did not change with the sintering temperature. Besides, its TCF value is acceptable compared with the other ULTCCs, such as Li_2MoO_4 sintered at 540 °C with a TCF−160 ppm/°C [12] and $Li_3AlB_2O_6$ sintered at 700 °C with a TCF −201 ppm/°C [32].

5. Conclusion

In conclusion, a novel HBO_2 ceramic was found to be well densified below 190 °C and possess high microwave dielectric performance with a relative permittivity ~2.12 ± 0.02, a Qf value ~32,700 ± 300 GHz and a TCF value ~ − 43 ± 3 ppm/°C. Compared with the traditional LTCCs, its sintering temperature is much more lower and makes it possible to design some novel inorganic-organic composite functional materials in the future. Besides, due to its water solubility, the HBO_2 slurry and tape might be processed via cheap water solution method in the future.

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