Sintering behavior and microwave dielectric properties of Ba$_{6-3x}$Nd$_{8+2x}$Ti$_{18}$O$_{54}$ (x = 2/3) ceramics coated by H$_3$BO$_3$-TEOS sol–gel

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A B S T R A C T

H$_3$BO$_3$–Si(OC$_2$H$_5$)$_4$ sol–gel was prepared and added as the sintering aid for Ba$_{6-3x}$Nd$_{8+2x}$Ti$_{18}$O$_{54}$ (x = 2/3, BNT) ceramic. The sintering behavior, microstructures, phase structures, and microwave dielectric properties were studied. The liquid phase was formed during the sintering process, which accelerated the process of reagent conversion and the mass-transport among the BNT powders. The sintering temperature of BNT ceramic was lowered from 1460 to 1075 °C. The H$_3$BO$_3$-TEOS sol–gel existed in the form of glass pellets, whose sizes were tens of nanometers, uniformly distributed around the BNT grains. By this method, perfect microstructures with BNT grains uniformly distributed in the ceramic matrixes were obtained, that were beneficial to the microwave dielectric properties of BNT ceramics. A ceramic composite which could be sintered well at 1075 °C and showed good microwave dielectric properties of ε_r = 73.8, Q_f = 8190 GHz and TCF = 47.2 ppm/°C was obtained when 2 wt.% H$_3$BO$_3$-TEOS sol–gel was added to the BNT ceramic. The mechanism for the low temperature sintering and the relationship between microwave dielectric properties and microstructures were discussed.

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1. Introduction

Recent progress in mobile and satellite telecommunications has increased the demands on the development of microwave components. Dielectric resonators with small size, low internal loss and good temperature stability at microwave frequency are required. Thus, there are three main requirements for dielectric resonator materials. First, the dielectric loss (tan δ, the ratio of the imaginary to the real part of complex permittivity) should be very low. Second, the dielectric constant (ε_r) should be high, to aid the miniaturization. Third, the temperature coefficient of the resonant frequency (TCF) should be approximately zero. The tungsten bronze-type like Ba$_{6-3x}$R$_{8+2x}$Ti$_{18}$O$_{54}$ (R = rare earth) ceramics, with superior microwave dielectric properties, have been extensively studied and widely used as electronic materials [1–6]. More recently, by applying low-temperature co-fired ceramic (LTCC) technology, passive elements have been integrated in monolithic, highly reliable, and robust LTCC modules that consist of several layers of ceramic substrates with integrated elements (inductors, capacitors, resonators), which are interconnected with three-dimensional strip-line circuitry [7]. Thus, low temperature sintering of this tungsten bronze-type like Ba$_{6-3x}$R$_{8+2x}$Ti$_{18}$O$_{54}$ ceramics have been studied [8–11] in order to replace noble metals like Pd or Pt by cheaper, highly conductive and low melting internal electrode metals such as silver (melting point = 961 °C) or copper (melting point = 1080 °C) in LTCC technology. However, it is difficult to lower the sintering temperature of Ba$_{6-3x}$R$_{8+2x}$Ti$_{18}$O$_{54}$ ceramics to below 1100 °C without the significant diminishing of their microwave dielectric properties. For microwave dielectrics, homogeneity of the phase composition and microstructure are very important to their dielectric properties. Thus, addition of nano-coating has become a new method to lower the sintering temperature of microwave dielectric. Wu et al. [12] have lowered the sintering temperature of BaNd$_2$Ti$_4$O$_{12}$ microwave ceramics using dissolvable copper salts, such as Cu(CH$_3$COO)$_2$, Cu(NO$_3$)$_2$ and CuSO$_4$, in order to prevent the agglomeration of dopants during sintering process. In this work, sol–gel mixture with [H$_3$BO$_3$]/[Si(OC$_2$H$_5$)$_4$] = 1 was prepared and added as sintering aids to lower the sintering temperature of Ba$_{6-3x}$Nd$_{8+2x}$Ti$_{18}$O$_{54}$ (x = 2/3, BNT) ceramic, whose sintering temperature was 1460 °C and microwave dielectric properties were ε_r = 82.5, quality factor (Q_f value, Q = 1/dielectri loss (tan δ), and f = resonant frequency) = 10,069 GHz, TCF = 71.1 ppm/°C [13]. The sintering temperature, microstructures, and microwave dielectric properties have been investigated. The mechanism for the low temperature sintering and the relationship between microwave dielectric properties and microstructures were discussed.

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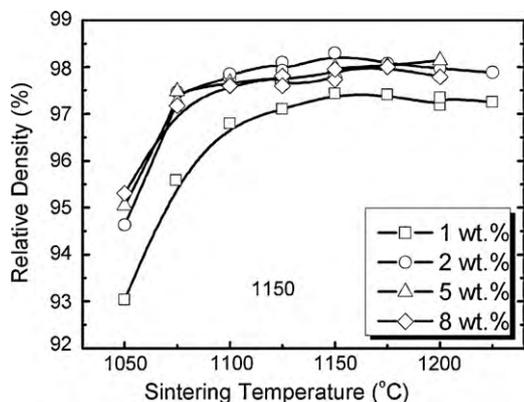E-mail address: plx1982@gmail.com (L.-X. Pang).

Fig. 1. Relative densities of BNT ceramics with 1–8 wt.% BS sol–gel addition as a function of sintering temperature.

2. Experimental

Sol–gel (0.4 mol/L) mixture with [H₃BO₃]/[TEOS] = 1 was prepared from tetraethyl orthosilicate (TEOS, Si(OC₂H₅)₄, ≥98.5%, Guo-Yao Co. Ltd., Shanghai, China) and orthoboric acid (H₃BO₃, ≥99.5%, Guo-Yao Co. Ltd., Shanghai, China). In the first step orthoboric acid solution was obtained by mixing the required amount of H₃BO₃ and deionized water. Then 0.1 M HNO₃ solution and half of the ethanol were added to the starting solution. This mixture was stirred for 30 min at room temperature to form solution-A. In another beaker, TEOS and the other half of the ethanol were mixed for 30 min to obtain solution-B. Then solution-A was slowly added into solution-B under stirring. After complete addition, the mixture was stirred for 4 h at room temperature and then sealed into a polypropylene container and gelled for 3 days.

The compound Ba$_{6-3x}$Nd$_{8+2x}$Ti$_{18}$O$_{54}$ ($x = 2/3$, BNT) was prepared by conventional solid-state reaction method. Mixed oxide powders were prepared from reagent grade BaCO₃ (≥99%, Guo-Yao Co. Ltd., Shanghai, China), Nd₂O₃ (≥99%, Guo-Yao Co. Ltd., Shanghai, China) and TiO₂ (>99%, Linghua Co. Ltd., Zhaoqing, China). The powders were weighed according to the composition and then milled with ZrO₂ balls (2 mm in diameter) for 4 h in ethanol. The mixture was dried and calcined at 1150 °C for 5 h, and then re-milled for 5 h. The dried powders were mixed with various volumes of H₃BO₃-TEOS sol–gel (the needed volumes of sol–gel were calculated to make sure that the contents of B₂O₃–2SiO₂ (BS) were 1, 2, 5, and 8 wt.% of the BNT powders), respectively. The mixtures were stirred at about 75 °C to dry and make the dried sol–gel coat on the BNT powders. Then the dried mixtures were granulated with PVA binder and pressed into cylinders (10 mm in diameter and 5 mm in height) under uniaxial pressure of 20 kN/cm². The cylinders were sintered in air at 1050–1225 °C for 3 h.

The bulk densities of BNT ceramics were measured by Archimedes' method and their theoretical densities were calculated using the equation [9]:

$$D = \frac{W_1 + W_2}{(W_1/D_1) + (W_2/D_2)}, \tag{1}$$

where W_1 and W_2 were the wt.% of BS and BNT in the mixture with densities D_1 and D_2, respectively. The microstructures of the as-fired surface and fracture surface of the samples were observed by scanning electron microscopy (SEM) (JSM-6360LV, JEOL, Tokyo, Japan). The crystalline phases of the samples were investigated using an X-ray diffractometry (XRD) with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). The dielectric behaviors at microwave frequency of the samples were measured by the TE$_{01\delta}$ shielded cavity method [14] using a network analyzer (8720ES, Agilent, Palo Alto, CA, USA) and a temperature chamber (DELTA 9023, Delta Design, Poway, CA, USA). The TCF was calculated by the following formula:

$$\text{TCF} = \frac{f_{85} - f_{25}}{f_{25} \times (85 - 25)}, \tag{2}$$

where f_{85} and f_{25} were the TE$_{01\delta}$ resonant frequencies at 85 and 25 °C, respectively.

3. Results and discussion

Fig. 1 shows the relative densities of BNT ceramics with 1–8 wt.% BS sol–gel addition as a function of sintering temperature. It is observed that the relative densities of BNT ceramics with 2–8 wt.% BS sol–gel addition could reach as high as 97% after sintering at 1075 °C, which means that the sintering temperature of BNT ceramic has been lowered to 1075 °C by 2–8 wt.% BS sol–gel addition.

Fig. 2 presents the microstructures of the specimens sintered at 1075 °C. It is seen that there are still a few pores in the BNT ceramic with 1 wt.% BS sol–gel addition (Fig. 2(a)). The specimens with 2–8 wt.% BS addition show dense microstructures (Fig. 2(b–d)). When the content of BS sol–gel addition increased to 8 wt.%, the superfluous liquid phase was separated out from the specimen and congregated on the surface of the sample during the sintering process (as shown in Fig. 2(f)). Meanwhile, it can be seen from the microstructures of the fracture surfaces that there are a lot of pellets with size of tens of nanometers distributed around the BNT grains. In conclusion, it is believed that during the cooling process a glass phase was formed. In this work, the BS sol–gel uniformly coated the BNT powders, so that the liquid phase of BS could be uniformly distributed around the BNT grains during the sintering process. Valant et al. [15,16] studied the mechanism of liquid-phase sintering. The following relationship [17] is used to describe the rate of reagent conversion:

$$\frac{dG}{d\tau} = KC_1 C_2 F, \tag{3}$$

where G is the degree of conversion, τ is the time, C_1 and C_2 are the concentrations of the reagents, and F is the surface contact area. In this work, the surface contact area F is significantly large because of the uniform distribution of the BS liquid phase around the BNT powders. Thus, the rate of reagent conversion increases significantly and the mass-transport between the BNT powders is accelerated because of the existence of the liquid phase. As a result, the sintering temperature of BNT is successfully lowered to 1075 °C. On the other hand, the rates of reagent conversion are uniform so that the grains of BNT keep the similar size in each ceramic matrix (as shown in Fig. 2).

As shown in Fig. 3, all of the XRD patterns of BNT ceramics with 1–8 wt.% BS sol–gel addition can be indexed as the tungsten bronze-like structure of Ba$_{6-3x}$Ln$_{8+2x}$Ti$_{18}$O$_{54}$ (JCPDS card no. 44-62). Even when the content of BS sol–gel is as high as 8 wt.%, no extra peaks are observed in the XRD pattern and BS phase is not found either, which is due to the fact that BS liquid phase is not crystallized during the cooling process and remains as the amorphous glass phase (as shown in Fig. 2). Meanwhile, as shown in the insert of Fig. 3, the angle of each diffraction peaks of BNT phase shifts little with BS sol–gel addition, which indicates that the lattice parameters of BNT phase were not influenced by BS addition. Furthermore BNT and BS sol–gel did not react with each other during the sintering process.

The dependence of microwave dielectric properties of BNT ceramics with various amount of BS sol–gel addition on sintering temperature is illustrated in Fig. 4. For the specimens in this work, there are three phases: BNT phase, BS glass phase, and the pores. The dielectric constant (ε_r) of mixture can be predicted by the well-known Lichtenecker empirical logarithmic rule [18]:

$$\ln \varepsilon_r = \sum_i v_i \ln \varepsilon_{ri}, \tag{4}$$

where v_i and ε_{ri} are the volume fractions and dielectric constant of each phase i, respectively. As shown in Fig. 4(a), the ε_r value of BNT + 2 wt.% BS ceramic is a little larger than that of BNT + 1 wt.% BS ceramic, which is due to the decrease in volume fraction of pores, whose dielectric constant is very small (≈ 1). As the content of the BS sol–gel addition increases to more than 2 wt.%, the influence of the BS glass phase increases, and the ε_r value of BNT ceramic decreases from 75.1 to 60.8 with the increasing BS content because of the small dielectric constant of the BS glass phase. The quality factor (Q_f value) of the BNT ceramics, as shown in Fig. 4(b), increases slightly with sintering temperature and decreases from 9100 to 7470 GHz as the content of BS sol–gel increases from 1 to 8 wt.%.
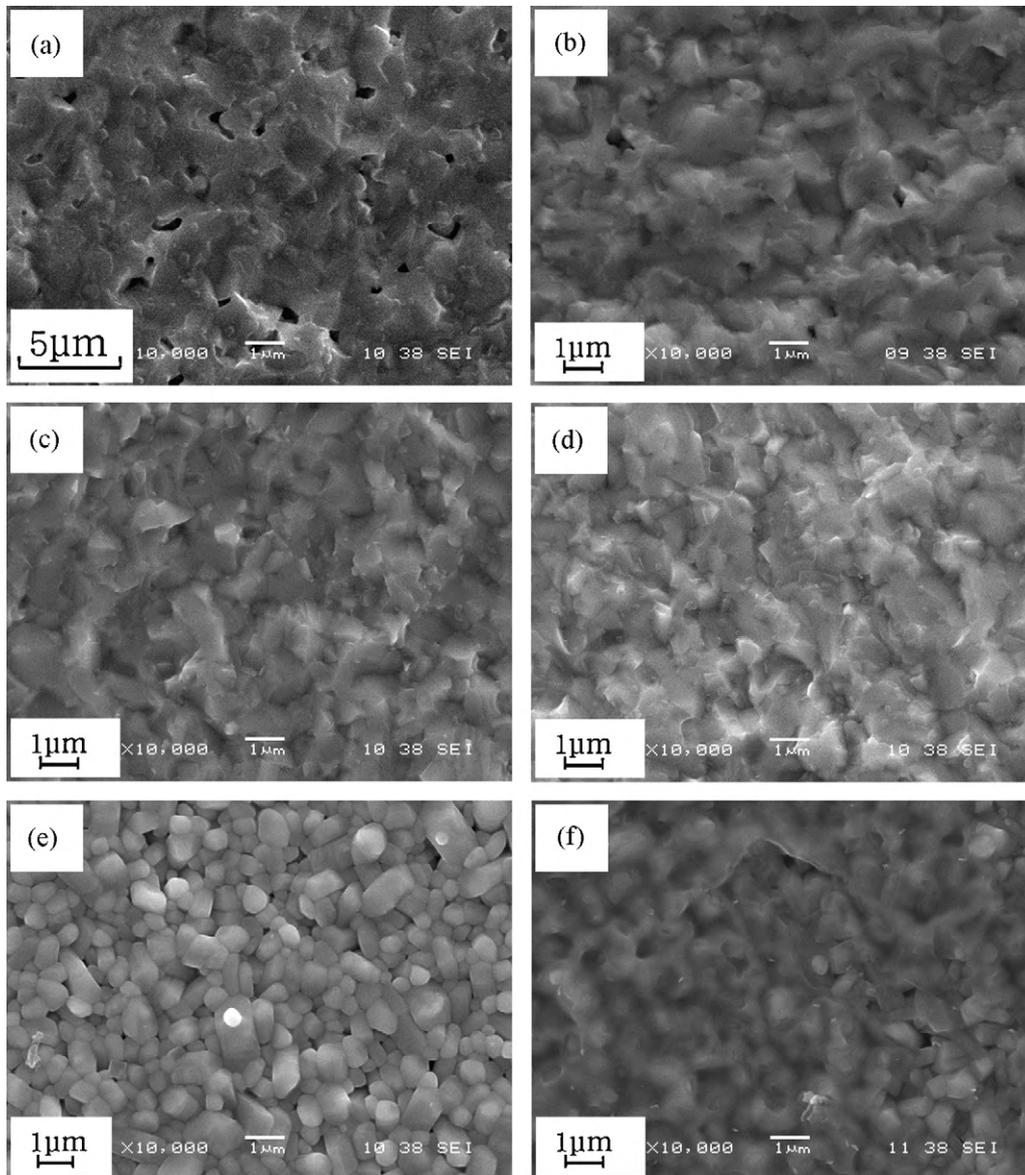
Fig. 2. SEM micrographs of fracture surfaces and as-fired surfaces of BNT ceramics with 1–8 wt.% BS sol–gel addition sintered at 1075 °C for 3 h: fracture surface of (a) 1 wt.%, (b) 2 wt.%, (c) 5 wt.%, (d) 8 wt.%; as-fired surface of (e) 5 wt.% and (f) 8 wt.%.
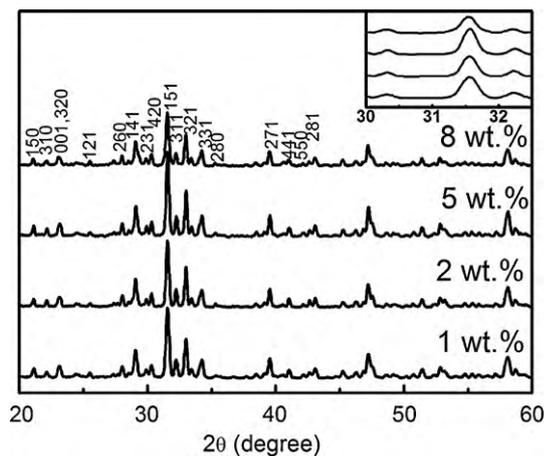
Fig. 3. XRD patterns of powders of BNT ceramics with various amount of BS sol–gel addition.

For dielectrics, there are three mechanisms that contribute to the dielectric loss at microwave frequencies: (1) losses due to anharmonic lattice forces in perfect crystals; (2) extrinsic losses due to porosity, secondary phases, grain boundaries, and inclusions in real homogeneous ceramics, and (3) losses in real but homogeneous crystals or crystallites caused by point defects, such as dopants, atoms, and vacancies [19]. In $Ba_{6-3x}Ln_{8+2x}Ti_{18}O_{54}$ (Ln = Sm, Nd and La) system, the Q_f value depends greatly on the local distortions at the A1- and the A2-sites [6]. In this work, the structure of the BNT phase is not influenced by BS addition, so that the decreasing of Q_f value is not related with the additional local distortions at the A1- or the A2-sites. In the BNT with BS sol–gel addition system, the main contribution to the dielectric loss is from extrinsic losses. The increase in Q_f value with sintering temperature is related to the decrease of porosity, and the decrease in Q_f value with the increasing content of BS addition is due to the increase of BS glass phase, which exists as the secondary phase. In many cases, the Q_f values of dielectrics diminish greatly because of the abnormal grain growth by the addition of glass or oxides with low melting temperature [9]. As discussed above, the rate of reagent conversion
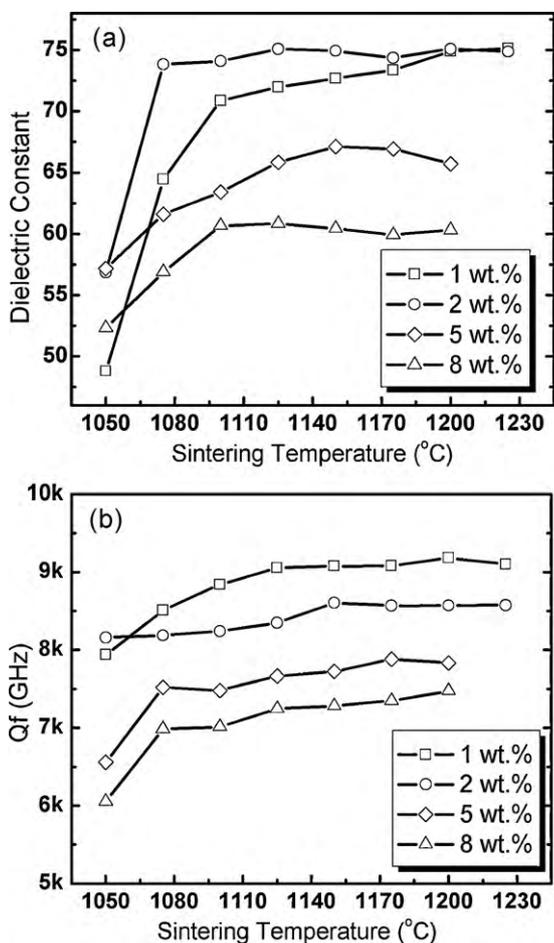
Fig. 4. Microwave dielectric properties ((a) dielectric constant and (b) Q_f value) of BNT ceramics with various amount of BS sol–gel as a function of sintering temperature.
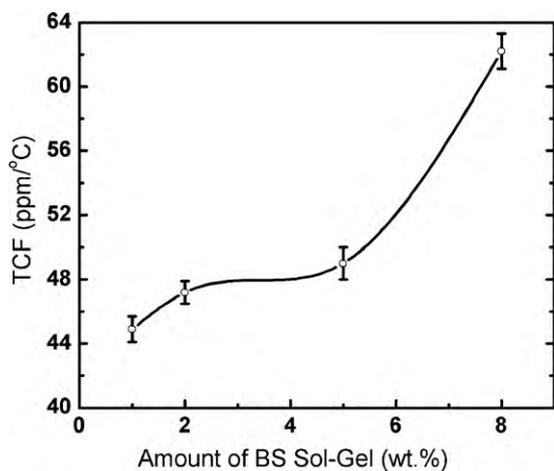

Fig. 5. TCF values of BNT ceramics as a function of amount of BS sol–gel.

is proportional to the content of liquid phase. When the sintering aids such as glass or oxides are added directly by mixing, the

distribution of the sintering aids is un-uniform, which causes the abnormal grain growth. In this work, the abnormal grain growth is prevented successfully by addition of BS glass in the form of sol–gel, so that the obtained BNT ceramics can remain relatively high Q_f values.

Fig. 5 shows the temperature coefficient of resonant frequency (TCF value) of BNT ceramics as a function of the amount of BS sol–gel. The TCF value here without BS sol–gel is about +42 ppm/°C. As the BS sol–gel content increased from 1 to 8 wt.%, the TCF value increased from +44.9 to +62.2 ppm/°C, which implies the TCF of BS glass might be a large positive value.

4. Conclusions

BS sol–gel was prepared from TEOS and H_3BO_3, and was added as the sintering aid for $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$, BNT) ceramics. A liquid phase was formed during the sintering process, which accelerated the process of reagent conversion and the mass-transport between the BNT powders, and the sintering temperature of BNT ceramic was lowered to 1075 °C. By this method, fine microstructures with uniform grains distributing in the ceramic matrixes were obtained. A ceramic composite which could be sintered well at 1075 °C and showed good microwave dielectric properties of $\varepsilon_r = 73.8$, $Q_f = 8190$ GHz and TCF = 47.2 ppm/°C was obtained when 2 wt.% H_3BO_3-TEOS sol–gel was added to the BNT ceramic.

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