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Sintering behavior and microwave dielectric properties of Bi_2O_3–ZnO–Nb_2O_5-based ceramics sintered under air and N_2 atmosphere

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Abstract

The sintering behavior and dielectric properties of the monoclinic zirconolite-like structure compound $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ (BZN) and $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ (BZNV, $x = 0.001$) sintered under air and N_2 atmosphere were investigated. The pure phase were obtained between 810 and 990 °C both for BZN and BZNV ceramics. The substitution of V_2O_5 and N_2 atmosphere accelerated the densification of ceramics slightly. The influences on microwave dielectric properties from different atmosphere were discussed in this work. The best microwave properties of BZN ceramics were obtained at 900 °C under N_2 atmosphere with $\varepsilon_r = 76.1$, $Q = 850$ and $Q_f = 3260$ GHz while the best properties of BZNV ceramics were got at 930 °C under air atmosphere with $\varepsilon_r = 76.7$, $Q = 890$ and $Q_f = 3580$ GHz. The temperature coefficient of resonant frequency τ_f was not obviously influenced by the different atmospheres. For BZN ceramics the τ_f was −79.8 ppm/°C while τ_f is −87.5 ppm/°C for BZNV ceramics.

Keywords: A. Sintering; B. Electron microscopy; C. Dielectric properties; D. Niobates

1. Introduction

Recently, low-temperature co-fired ceramic (LTCC) technology has played a more and more important role in the advanced packaging and multilayered integrated circuit [1]. In order to co-fire with low-melting-point conductors, i.e., silver and copper electrode, low-firing-microwave dielectric materials with high dielectric constants ε_r, high Q_f values and small temperature coefficients of the resonant frequency τ_f are needed.

Bi_2O_3–ZnO–Nb_2O_5 (BZN)-based pyrochlore ceramics were first reported in 1970s by Chinese engineers for low-firing temperature multilayer capacitors [2]. Recently, this system attracts more and more attentions due to its low sintering temperatures and excellent microwave dielectric properties. $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ ceramics with a dielectric constant of 80, dielectric losses (tan δ) as low as 1×10^{-4} at frequency of 1 MHz, were reported in 1997 [3,4]. The sintering behavior and microwave dielectric properties of low-temperature sintered $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ had been reported recently by Choi et al. [5] The $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ ($x = 0.001$) sintered at 850 °C for 2 h exhibited good microwave dielectric properties: $Q_f = 3800$ at 6 GHz, $\varepsilon_r = 78.6$ and this composition showed compatibility with silver inner electrode.

Besides silver electrode, the copper electrode is also a very important low-melting-point conductor. Considering the co-firing of different kinds of ceramics and reaction of many ceramics with Ag, such as $BiNbO_4$ [6,7], it is important to study the co-firing between Cu and ceramics. The copper electrode must be co-fired with ceramics under inert or reductive atmospheres. So the study of the microwave dielectric properties of ceramics sintered under N_2 or other atmosphere is necessary. N_2 atmosphere seems to be of benefit to the densification of ceramics. $BiNbO_4$ system ceramics sintered under nitrogen atmosphere have been studied and some good results of microwave dielectric properties were obtained [8,9]. The nitrogen atmosphere may improve or deteriorate the microwave dielectric properties for different compositions. But the study on sintering behavior and microwave dielectric properties of ceramics sintered under nitrogen atmosphere were not reported about BZN system before. In this work, both the traditional compositions of $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ (BZN) and

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$Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ (BZNV, $x = 0.001$) compositions were chosen and sintered under air and N_2 atmosphere. The sintering behavior and microwave dielectric properties were studied in detail.

2. Experimental procedure

The powders were prepared by conventional mixed oxide method. Bi_2O_3 (>99%, Shu-Du Powders Co. Ltd., China), ZnO, Nb_2O_5 and V_2O_5 (>99%, Zhu-Zhou Harden Alloys Co. Ltd., China) powders with 99.9% purity were weighed according to the compositions $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ (β-BZN) and $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ (β-BZNV, $x = 0.001$). The mixed powders were mixed for 4 h with stabilized zirconia media and ethanol then were calcined at 750 °C for 4 h and ball-milled again for 5 h. The milled powders were dried and pressed into disks 10 mm in diameter and 5 mm in thickness under a pressure about 17 kN/cm^2. Green samples were sintered at 810–990 °C for 2 h both in air and N_2 atmosphere with a heating rate of 3 °C/min.

The bulk density of the sintered specimens was determined by the Archimedes method. After surface polished, the crystalline structures of the samples were investigated using x-ray diffractometry with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometry, Japan). The surface of sintered specimens was observed by a SEM (JEOL JSM-6460, Japan).

Dielectric behaviors at microwave frequency were measured by the $TE_{0\ 1\ \delta}$ shielded cavity method using a network analyzer (8720ES, Agilent, USA) and a temperature chamber (DELTA 9023, Delta Design, USA). The temperature coefficients of resonant frequency τ_f value was calculated by the formula:

$$\tau_f = \frac{f_T - f_0}{f_0(T - T_0)} \quad (1)$$

where f_T, f_0 were the resonant frequencies at the measuring temperature T and RT (25 °C), respectively.

3. Results and discussion

Fig. 1 shows the XRD patterns of ceramics sintered at various temperatures and atmospheres. Only the pure β-BZN phase was observed in all the samples. The sintering temperature, atmospheres and substitution of V^{5+} have no significant influence on the phase equilibrium.

The SEM photos of ceramics sintered under different atmospheres are shown in Fig. 2. The homogeneously fine microstructures with almost no pores are revealed for β-BZN ceramics sintered at 960 °C under air and N_2 atmospheres as shown in Fig. 2(a) and (c). The grain shapes are similar. The average grain sizes of these two ceramics were calculated from the line intercept method and all of them are distributed around 2–3 μm. This suggests that the different oxygenic partial pressure has no apparent influence on grain growth of pure β-BZN. Fig. 2(b) shows the SEM photos of β-BZNV ceramics sintered at 900 °C under air atmosphere. The average size lies between 0.8 and 1.25 μm. For β-BZNV ceramics sintered

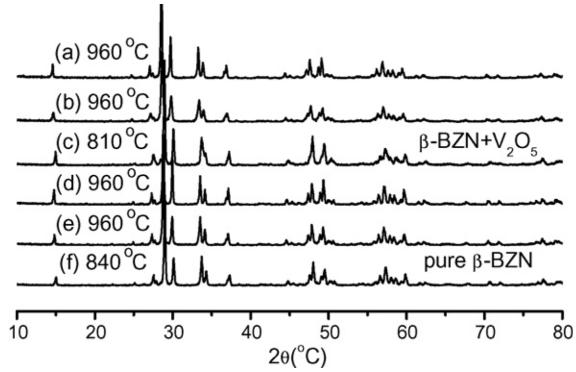

Fig. 1. XRD patterns for β-BZNV ceramics sintered at 960 °C under N_2 (a), 960 °C (b) and 810 °C (c) under air, for β-BZN ceramics sintered at 960 °C (d) under N_2, 900 °C (e) and 840 °C (f) under air.

under N_2 atmosphere, the average size is about 0.5–1.25 μm and the size distribution is not homogeneous as shown in Fig. 2(d).

The densities of β-BZN ceramics sintered at various temperatures and atmospheres are shown in Fig. 3. The density reached the saturated value at 840 °C for both pure and substituted samples sintered under air and N_2 atmospheres. The ceramics seemed to be densified more easily under N_2 atmosphere (as shown in Fig. 3 at S.T. = 810 °C). The oxygen vacancy increased as the decrease of oxygenic partial pressure in the atmosphere and its influence to density was as following:

$$\rho_{N_2} = \rho_O - [V_{\ddot{O}}] \times M_O \quad (2)$$

where the M_O is the atomic weight of oxygen and the $[V_{\ddot{O}}]$ is the density of oxygen vacancy. As the oxygenic partial pressure is decreased, the density of samples sintered under N_2 atmosphere is a little smaller than that under air atmosphere. The average difference of the densities between densified ceramics sintered under air and N_2 atmosphere was about 0.02 g/cm^3. The calculated density of $[V_{\ddot{O}}]$ is about 7.5×10^{20}/cm^3. And the ratio of the density of $[V_{\ddot{O}}]$ to that of oxygen atoms in a intact crystal is about 0.016, which means that there was about 0.9 oxygen vacancy in a unit cell of $Bi_{16}(Zn_{1/3}Nb_{2/3})_{16}O_{56}$.

The dielectric constant of β-BZN ceramics is shown in Fig. 4. It has the similar trend with that of the density. Influence from pores to permittivity was thought to dominate its change of trend. According to the ionic polarizability reported by Shannon [10], there is

$$\alpha[BiNbO_4]_{N_2} = \alpha[BiNbO_4]_{air} - [V_{\ddot{O}}] \times \alpha(O^{2-}) \quad (3)$$

where $\alpha(O^{2-})$ is the polarizability of O^{2-}. So the permittivity of samples sintered under N_2 atmosphere was a little smaller than that of sample sintered under air atmosphere.

The Q_f values of β-BZN ceramics as a function of sintering temperatures and atmospheres are shown in Fig. 5. The microwave dielectric loss includes two intrinsic part and extrinsic part. Mostly the extrinsic losses, caused by the lattice defect (e.g., impurity, cavity, substitution, grain boundaries, size and shapes of grains, second phase, pores, etc.), would dominate the change of Q_f value. Here, the extrinsic losses

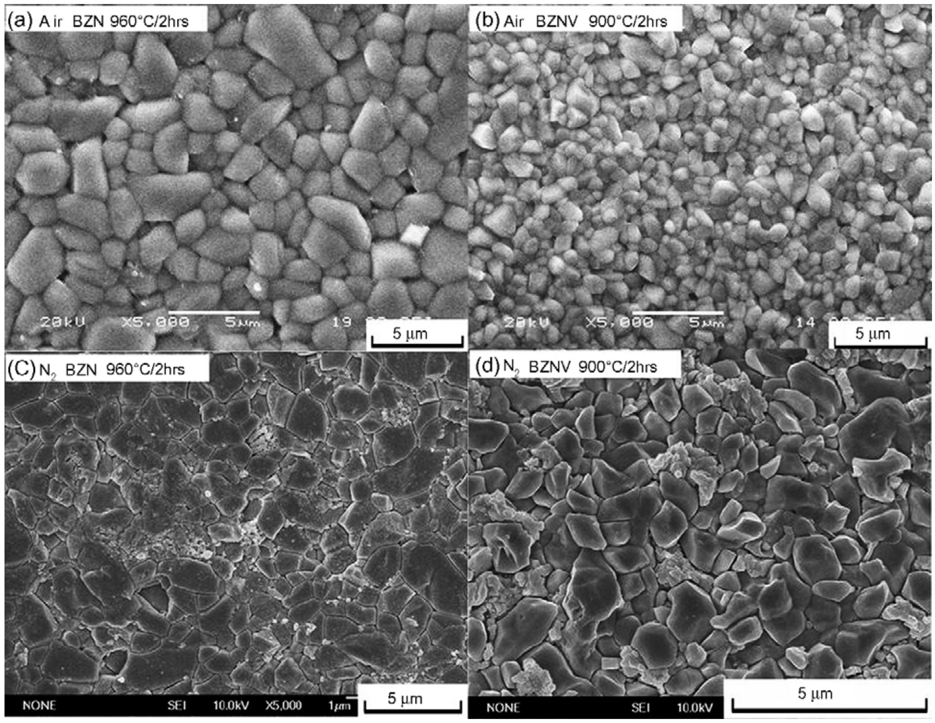

Fig. 2. SEM micrographs for ceramics sintered at various temperatures.

could be attributed to the differences in shape and size of grains, caused by different sintering temperatures and oxygen partial pressures, O^{2-} vacancy and the substitution of V^{5+}. For pure β-BZN ceramics as shown in Fig. 5(a), the trends of change in Q_f values with sintering temperature are almost the same for ceramics sintered under different atmospheres. This trend could be simply explained in the following. As sintering temperature was increased, firstly, the increase in densification of ceramic and the growth of grain can improve the Q_f values. Then, at the further secondary growth of grains, the subsequent unhomogeneity of grains deteriorates the Q_f values. Typically, the Q_f values of pure BZN ceramics sintered under N_2 atmosphere are not much higher than that sintered under air atmosphere. This phenomenon is similar as that in $BiNbO_4$ ceramics reported by Wang et al. [8] and could be attributed to the influence of oxygen vacancy and microstructure.

Fig. 5(b) shows the Q_f values of β-BZNV ceramics as a function of sintering temperatures and atmospheres. The Q_f values of β-BZNV ceramics are not much higher than that of β-BZN ceramics and it corresponds well with the results reported by Choi et al. [5]. Generally, the Q_f values for β-BZNV ceramics sintered under N_2 atmosphere are not much lower than that of ceramics sintered under air atmosphere and this shows a different trend from that of β-BZN ceramics. This could be attributed to the narrower and broader distribution of grain size for the ceramics sintered under N_2 atmosphere. The total ratio of the grain boundaries would increase as a decrease in the average grain size which would contribute significantly to extrinsic dielectric loss [11]. Some possible reasons also caused the deteriorations of Q_f values. First the volatilization of vanadium at high temperature must be considered. Then in the N_2 atmosphere, the deoxidization of V^{5+} to V^{3+} and V^{4+} also

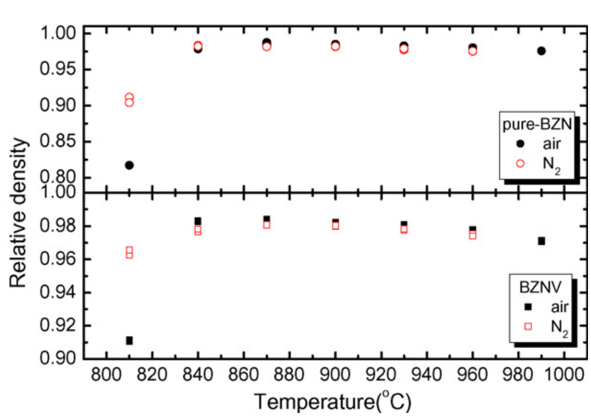

Fig. 3. Bulk densities of ceramics sintered at various temperatures and atmospheres.

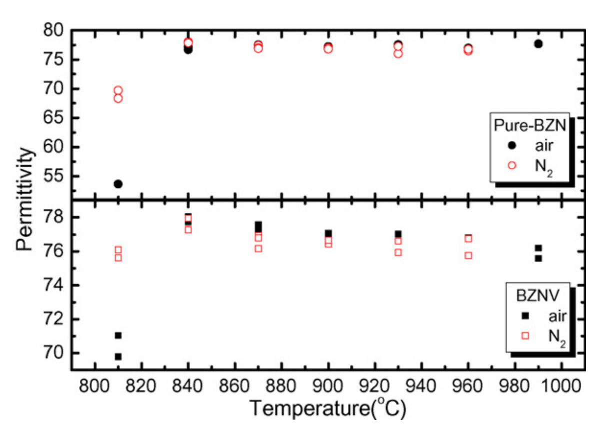

Fig. 4. Dielectric constants of β-BZN (a) and β-BZNV (b) ceramics sintered at various temperatures and atmospheres.

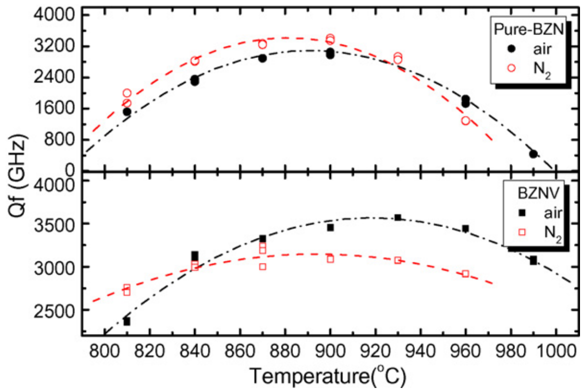

Fig. 5. Q_f values ceramics sintered at various temperatures and atmospheres.

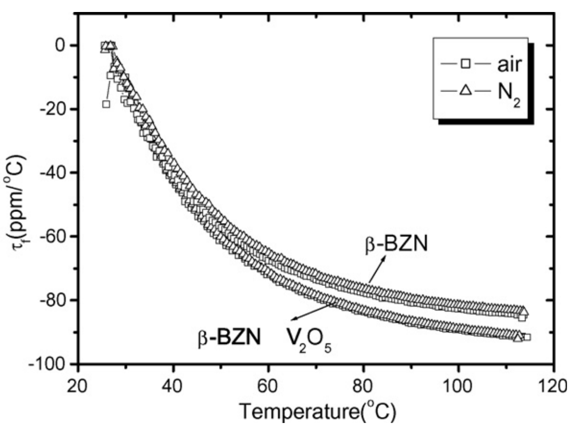

Fig. 6. Temperature coefficient of resonant frequency as a function of temperatures.

could not be neglected. The process of V_2O_3 and VO_2 substituting for Nb_2O_5 can be summarized in the following incorporation reaction:

$$V_2O_3 \overset{Nb_2O_5}{\longrightarrow} 2V''_{Nb} + 3O_O + 2V_O^{\cdot\cdot} \quad (4)$$

$$2VO_2 \overset{Nb_2O_5}{\longrightarrow} 2V'_{Nb} + 4O_O + V_O^{\cdot\cdot} \quad (5)$$

where $V_O^{\cdot\cdot}$ is the oxygen vacancy. Then there will be some tendency for the more mobile vacancies to be attracted to the vicinity of the oppositely charged impurity center, V'_{Nb} and V''_{Nb}, respectively. Although the $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ was designed assuming the substitution of V^{5+} for the Nb^{5+}, whether the V^{5+} occupied the position of Nb^{5+} is not very clear. From our previous work [12], with an increase in substitution of V^{5+} for the Nb^{5+} in $Bi(Nb_{1-x}V_x)O_4$ system, the second phase of $BiVO_4$ with weak trace was revealed. From the work of Choi et al. [5], the second phase of $Bi_4V_2O_{11}$ and $BiNbO_4$ were found in $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ with $x \geq 0.01$. Thus, some other phases with very small amount might be formed here causing to deteriorate the Q_f values.

The temperature coefficients of resonant frequency τ_f as a function of testing temperatures are shown in Fig. 6. The τ_f of samples sintered under air and N_2 atmospheres have no remarkable difference. The τ_f value of substituted BZN is about −84.7 ppm/°C at 85 °C, which is a slight higher than that of pure BZN (−78 ppm/°C).

4. Conclusions

For both $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ and $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ ($x = 0.001$) compositions, the ceramics could be well densified under air and N_2 atmospheres. The permittivity as a function of sintering temperatures has a similar trend with that of densities. The oxygen vacancies cause a small decrease of density and permittivity. At microwave region, the low oxygen partial pressure results a increase of the Q_f value for pure $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ ceramics. But for $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ ceramics, the more negative influence on the losses deteriorating from the extrinsic contribution might be caused by the inhomogeneity of grains for ceramics sintered under N_2 atmosphere. The temperature coefficients of resonant frequency are big in negative direction in the two compositions and need further modification.

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References

[1] S.T. Ishizaki, M. Fujita, H. Kagata, T. Uwano, Very small dielectric planar filter for portable telephones, IEEE Trans. Microwave Theory Tech. 42 (11) (1994) 2017–2022.
[2] Z.P. Wang, S.Y. Zhang, No lead low-fired multilayer ceramic capacitor (MLC) dielectric materials, Electron. Compon. Mater. (Chin.) 1 (1) (1979) 11–18.
[3] D.P. Cann, C.A. Randall, T.R. Shrout, Investigation of the dielectric properties of bismuth pyrochlores, Solid State Commun. 7 (1996) 529–534.
[4] X.L. Wang, H. Wang, X. Yao, Structures, phase transformations, and dielectric properties of pyrochlores containing bismuth, J. Am. Ceram. Soc. 80 (10) (1997) 2745–2748.
[5] G.K. Choi, D.W. Kim, S.Y. Cho, K.S. Hong, Influence of V_2O_5 substitutions to $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ pyrochlore on sintering temperature and dielectric properties, Ceram. Int. 30 (2004) 1187–1190.
[6] S.Y. Cho, H.J. Youn, D.W. Kim, T.G. Kim, K.S. Hong, Interaction of $BiNbO_4$-based low-firing ceramics with silver electrodes, J. Am. Ceram. Soc. 81 (1998) 3038–3040.
[7] M. Valant, D. Suvorov, Chemical compatibility between silver electrodes and low-firing binary-oxide compounds: conceptual study, J. Am. Ceram. Soc. 83 (11) (2000) 2721–2729.
[8] Zh.W. Wang, X. Yao, L.Y. Zhang, CeO_2-modified $BiNbO_4$ microwave ceramics sintered under atmosphere, Ceram. Int. 30 (2004) 1329–1333.
[9] Y. Yang, Sh.H. Ding, X. Yao, Influences of Fe_2O_3 additives on the dielectric properties of $BiNbO_4$ ceramics under different sintering atmosphere, Ceram. Int. 30 (2004) 1341–1345.
[10] R.D. Shannon, Dielectric polarizabilities of ions in oxides and fluorides, J. Appl. Phys. 73 (1993) 348–366.
[11] N. Ichinose, T. Shimada, Effect of grain size and secondary phase on microwave dielectric properties of $Ba(Mg_{1/3}Ta_{2/3})O_3$ and $Ba([Mg,Zn]_{1/3}Ta_{2/3})O_3$ systems, J. Eur. Ceram. Soc. 26 (2006) 1755–1759.
[12] D. Zhou, H. Wang, X. Yao, Y. Liu, Microwave dielectric properties of low-firing $BiNbO_4$ ceramics with V_2O_5 substitution, J. Electroceram., in press.