Sintering behavior and microwave dielectric properties of Bi$_2$O$_3$–ZnO–Nb$_2$O$_5$-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$_{2/3}$)$_2$O$_7$ (BZN) and Bi$_2$(Zn$_{1/3}$Nb$_{2/3}$)$_2$O$_7$ ($x = 0.001$) 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$_2$O$_5$ 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 $\varepsilon_r = 76.1$, $Q_f = 850$ and $Q_f = 3260$ GHz while the best properties of BZNV ceramics were got at 930 °C under air atmosphere with $\varepsilon_r = 76.7$, $Q_f = 890$ and $Q_f = 3580$ GHz. The temperature coefficient of resonant frequency $\tau_f$ was not obviously influenced by the different atmospheres. For BZN ceramics the $\tau_f$ was $-79.8$ ppm/°C while $\tau_f$ 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 $\varepsilon_r$, high $Q_f$ values and small temperature coefficients of the resonant frequency $\tau_f$ are needed.

Bi$_2$O$_3$–ZnO–Nb$_2$O$_5$ (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$_{2/3}$)$_2$O$_7$ ceramics with a dielectric constant of 80, dielectric losses (tan $\delta$) as low as $1 \times 10^{-4}$ 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$_{2/3}$)$_2$O$_7$ had been reported recently by Choi et al. [5] The Bi$_2$(Zn$_{1/3}$Nb$_{2/3}$–$x$V$_x$)$_2$O$_7$ ($x = 0.001$) 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$_{2/3}$)$_2$O$_7$ (BZN) and
2. Experimental procedure

The powders were prepared by conventional mixed oxide method. Bi₂O₃ (>99%, Shu-Du Powders Co. Ltd., China), ZnO, Nb₂O₅ and V₂O₅ (>99%, Zhu-Zhou Harden Alloys Co. Ltd., China) powders with 99.9% purity were weighed according to the compositions Bi₂(ZnₓNb(2/3−ₓ)Vₓ)₂O₇ (β-BZN, x = 0.001) compositions were chosen and sintered under air and N₂ atmosphere. The sintering behavior and microwave dielectric properties were studied in detail.

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 V⁵⁺ have no significant influence on the phase equilibrium.

The SEM photos of ceramics sintered under different atmospheres are shown in Fig. 2. The homogeneous fine microstructures with almost no pores are revealed for β-BZN ceramics sintered at 960 °C under air and N₂ 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-BZN ceramics sintered at 900 °C under air atmosphere. The average size lies between 0.8 and 1.25 μm. For β-BZN ceramics sintered under N₂ 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 N₂ atmospheres. The ceramics seemed to be densified more easily under N₂ 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:

\[
\rho_{N_2} = \rho_0 - \frac{\rho_{V_0} \times M_O}{V_0} \tag{2}
\]

where \(M_O\) is the atomic weight of oxygen and the \(\rho_{V_0}\) is the density of oxygen vacancy. As the oxygenic partial pressure is decreased, the density of samples sintered under N₂ atmosphere is a little smaller than that under air atmosphere. The average difference of the densities between densified ceramics sintered under air and N₂ atmosphere was about 0.02 g/cm³. The calculated density of \(\rho_{V_0}\) is about 7.5 × 10²⁰/cm³. And the ratio of the density of \(\rho_{V_0}\) 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 Bi₁₆(Zn₁₆Nb₃₂V₁₆)₁₆O₅₆.

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

\[
\alpha(BiNbO₃)_{N_2} = \alpha(BiNbO₃)_{air} - \left[\rho_{V_0}\right] \times \alpha(O^{2−}) \tag{3}
\]

where \(\alpha(O^{2−})\) is the polarizability of O²⁻. So the permittivity of samples sintered under N₂ atmosphere was a little smaller than that of sample sintered under air atmosphere.

The Qᵢ 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 Qᵢ value. Here, the extrinsic losses...
could be attributed to the differences in shape and size of grains, caused by different sintering temperatures and oxygen partial pressures, $O_2^{-2}$ vacancy and the substitution of $V^{5+}$. For pure $\beta$-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 $\beta$-BZNV ceramics as a function of sintering temperatures and atmospheres. The $Q_f$ values of $\beta$-BZNV ceramics are not much higher than that of $\beta$-BZN ceramics and it corresponds well with the results reported by Choi et al. [5]. Generally, the $Q_f$ values for $\beta$-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 $\beta$-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...
The temperature coefficients of resonant frequency \( f \) as a function of testing temperatures are shown in Fig. 6. The \( f \) values for samples sintered at various temperatures and atmospheres.

\[
\begin{align*}
V_2O_3 & \rightarrow 2V_{Nb} + 3O_0 + 2V_O \\
2VO_2 & \rightarrow 2V'_{Nb} + 4O_0 + V_O
\end{align*}
\]

where \( V_O \) 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 \( Bi_2(Zn_{1/3}Nb_{2/3})_2O_7 \) 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 \( Bi_2V_2O_7 \) and \( BiNbO_4 \) were found in \( Bi_2(Zn_{1/3}Nb_{2/3})_2O_7 \) with \( x \geq 0.01 \). Thus, some other phases with very small amount might be formed here causing to deteriorate the \( Q_t \) values.

The temperature coefficients of resonant frequency \( \tau_f \) as a function of testing temperatures are shown in Fig. 6. The \( \tau_f \) of samples sintered under air and \( N_2 \) atmospheres have no remarkable difference. The \( \tau_f \) value of substituted \( BZN \) is about \(-8.47 \) 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 \( Bi_2(Zn_{1/3}Nb_{2/3-\gamma}V_x)_2O_7 \) \((x = 0.001)\) 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 \( Q_t \) value for pure \( Bi_2(Zn_{1/3}Nb_{2/3})_2O_7 \) ceramics. But for \( Bi_2(Zn_{1/3}Nb_{2/3-\gamma}V_x)_2O_7 \) 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