

Interfacial behaviour between $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7 \cdot 0.02\text{V}_2\text{O}_5$ and Ag

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Abstract

The interfacial behavior between $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7 \cdot 0.02\text{V}_2\text{O}_5$ (BZN-V) dielectric and silver was investigated by using X-ray diffractometer, scanning electronic microscopy, and electronic probe microanalyzer (EPMA). No new crystalline phase was found after firing the mixture of BZN-V and silver powder at 850 °C for 1 h. However, silver migration was observed when BZN-V was cofired with a silver electrode under the same condition. A diffusion distance of 620 μm was measured by EPMA. A eutectic reaction between silver and V_2O_5 is proposed for the mechanism of the silver migration.

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1. Introduction

The demands for miniaturization in the microwave communication technologies require continuing discovery and development of new materials. Most conventional ceramics that have excellent microwave dielectric properties such as BMT ($\text{BaMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$), BNT ($\text{BaO-Nd}_2\text{O}_3\text{-TiO}_2$), etc. must have sinterability above 1300 °C. Because of the high sintering temperature, Ag–Pd electrode is the only choice for multilayer ceramic components (MLCCs). In the microwave frequency range, the dielectric loss of component is mostly attributed to the electrode. The good conductivity of the electrode is important for MLCCs. Thus, it is desirable to replace the poor conductivity and high cost of Ag–Pd electrode with the better properties and lower cost of silver electrodes. However, the low melting temperature (961 °C) of silver and the silver migration problem need to be addressed when silver is cofired with microwave ceramics. Many recent developments have been dedicated to low sintering ceramics. The degrading of dielectric properties could be reduced or eliminated from the silver diffusing toward dielectrics^{1–4} by using active components that react with silver or by a buffer layer that stops silver migration.

Recently, $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ (BZN) has emerged as a good microwave material because it exhibits high dielectric constant and low temperature coefficient of

resonance frequency (τ_f).^{5–11} When 2 mol% V_2O_5 is added to BZN (BZN-V), the product can be sintered at 850 °C. To determine whether the BZN-V can be cofired with silver or not, we have investigated the interfacial behavior between the BZN-V and silver to solve the silver migration problem.

2. Experimental

Reagent grade oxide powders with a molar ratio of 1.00:1.22:1.00 of Bi_2O_3 , ZnO, and Nb_2O_5 (99.9% purity each, Alfa Chemicals, USA) were used to prepare cubic pyrochlore BZN using the conventional mixed solid method followed by calcination at 900 °C for 4 h. After the crystalline phase of calcined BZN powder was confirmed via the literature data, 2 mol% V_2O_5 powder was added as a sintering aid (BZN-V). The BZN-V powder was characterized by light scattering (Mastersizer 2000, Malvern Instruments, UK) for particle size, B.E.T for surface area (Micromeritics, ASAP2000 BET, USA), inductively coupled plasma-mass spectrometer (ICP-Mass, Sciex Elan 5000, Perkin-Elmer, USA) for chemical composition, and X-ray diffractometer (XRD, PW 1830, Philips, Nederland) for the crystalline structure. The BZN-V powder was pressed at 42 MPa to form tablets (10 mm diameter), and sintered at 850 °C for 1 h. The dielectric properties of sintered BZN-V tablets were evaluated by dielectric analyzer (LCR 3260A, Wayne Kerr, UK) and network analyzer (Hewlett Packard, 8722ES Network Analyzer, USA).

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For the silver migration study, two kinds of samples were prepared. One type of samples was prepared by mixing BZN-V with various amount of silver (0–10 wt.%) and sintered at 850 °C for 1 h. The fired samples were analyzed by XRD. Another type of samples was prepared by printing silver electrode over dense BZN-V tablets and cofiring the products at various temperatures (700–850 °C) for 1 h. The diffusion distance and concentration of silver were determined by electronic probe micro-analyzer (EPMA). The microstructures of sintered samples were evaluated by scanning electronic microscopy equipped with EDS (SEM, JSM-T100, Joel, Japan).

3. Results and discussion

The BZN-V has been prepared by the solid mixing method. The surface area and particle size of the BZN-V powder were 5.08m²/g, 0.53 μm respectively, measured by light scattering and B.E.T. Table 1 indicated that the content of bismuth in the BZN-V powder was reduced after calcinations at 900 °C for 4 h. This might be due to the volatilization of bismuth. However, the cubic pyrochlore phase of Bi_{1.5}ZnNb_{1.5}O₇ was stable and observed according to the XRD analysis (Fig. 1). The SEM microstructure of BZN-V sintered at 850 °C for 1 h showed that the average crystalline size of BZN is in the range of 0.5–1.0 μm. The EDS analysis of sintered samples indicated the existence of Zn-rich phase that was from the 22 mole% excess ZnO used in the

preparation of BZN-V. The EDS results also showed that the presence of V-rich phase located at the grain boundaries that confirmed the sintering aid role of V₂O₅.

The dielectric properties of sintered BZN-V at 1 MHz and 2.95 GHz are summarized in Tables 2 and 3, respectively and compared with literature data.^{12–14} Our data are in agreement with them except for the high quality factor data of Wu.⁵ A high dielectric constant (165 at 1MHz) of BZN-V reveals that the material has a potential to reduce the size of microwave component significantly. Fig. 2 shows that the dielectric relaxation of the material occurred between 40 and 100 K, and shifted to a higher temperature when the frequency was increased. The results are consistent with the report of Nino et al.¹⁴ The oxide pyrochlore has a general formula of A₂B₂O₇. Margen et al.¹⁵ has shown experimentally, the Zn²⁺ was distributed between A site and B site in their (Bi_{1.5}Zn_{0.5})(Sb_{1.5}Zn_{0.5})O₇ pyrochlore. In the case of Bi_{1.5}ZnNb_{1.5}O₇, the size of Zn²⁺ (CN=8, 0.90

Table 1
Molar ratio of BZN-V measured by ICP-mass spectrometry

Sample	Bi	Zn	Nb	V
Before calcine	2.00	1.22	2.00	0.04
After calcine at 900 °C, 1 h	1.57	1.22	2.00	0.04

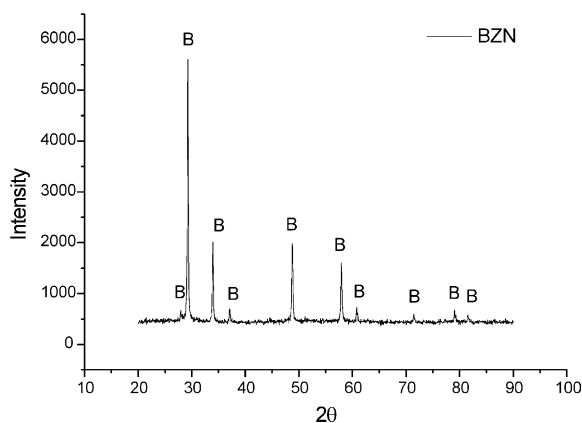


Fig. 1. XRD of BZN powder calcined at 900 °C for 4 h (B: BZN peak).

Table 2
Dielectric properties of BZN-V compared with literature data at low frequency

Composition	f (Hz)	k	Tan δ	Ref.
Bi ₂ ZnNb ₂ O ₉	100 K	135.00	–	8
Bi _{1.5} ZnNb _{1.5} O ₇	1 M	155.00	1.00E-4	12
Bi _{1.5} ZnNb _{1.5} O ₇	1 M	152.00	3.00E-4	13
Bi _{1.5} ZnNb _{1.5} O ₇	100 K	140.00	2.00E-3	14
Bi _{1.5} ZnNb _{1.5} O ₇	1 M	165.00	3.56E-4	Our data

Table 3
Dielectric properties of BZN-V compared with literature data at high frequency

Composition	f (Hz)	k	Q×f	Ref.
Bi ₂ ZnNb ₂ O ₉	–	65	63,000	5
Bi _{1.5} ZnNb _{1.5} O ₇	1.00 G	148	14	14
Bi _{1.5} ZnNb _{1.5} O ₇	2.95 G	150	118	Our data

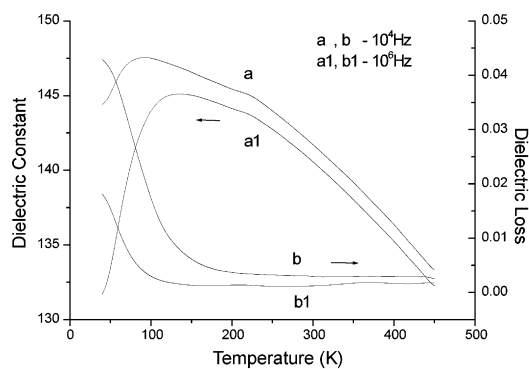


Fig. 2. Dielectric constants and dielectric losses of BZN-V from 40–450 K at 10⁴ and 10⁶ Hz, respectively.

Å; CN=6, 0.74 Å) is in between Bi^{3+} (1.17 Å) and Nb^{5+} (0.64 Å), a heterogeneous occupation of Zn ions between A site and B site is expected. The possible heterogeneous occupation of Zn ions in pyrochlore BZN will result in partially distortion of its microstructure that may be the contribution to its relaxation peak and responsible for the low quality factor of 118 at 2.95 GHz in our sample.

According to the XRD study, it was interesting to observe that no new crystalline phase was formed (Fig. 3) when the BZN-V was mixed with silver powder and sintered at 850 °C for 1 h. The results indicated that silver did not enter into the lattice structure of BZN. However, after cofiring dense BZN-V with silver electrode at various temperatures of 700, 750, 800 and 850 °C, SEM photos showed channel voids near to the interface (Fig. 4). At the high temperature of 850 °C, the situation was more serious than that at the low temperature of 700 °C. From EPMA studies, the distance of silver migration toward BZN-V was increased from 335 to 620 μm when the temperature was increased from 700 to 850 °C (Table 4). We suspected that the V_2O_5 had reacted with silver. Therefore, we cofired the dense neat

BZN (without V_2O_5 , sintered at 1100 °C for 4 h) with silver electrode at 850 °C for 1 h. The SEM photo (Fig. 5) shows no channel voids and the EPMA study indicates no silver migration. The results suggested that silver had reacted with V_2O_5 to form eutectic liquid phases. When they were evaporated off at sintering temperature, channel voids were observed at the grain boundaries of BZN. The DTA study of a mixture of silver and V_2O_5 was performed to prove the hypothesis. The DTA peaks at 469 °C, 563 °C, 735 °C (Fig. 6) were observed those are corresponded to the eutectic liquid phases of silver and V_2O_5 from their phase diagram.¹⁶

Table 4

EPMA results of BZN-V dense disk cofired with Ag electrode at various temperatures for 1 h

Sintering temperature (°C)	Ag diffusion distance (μm)
850	620
800	450
750	360
700	335

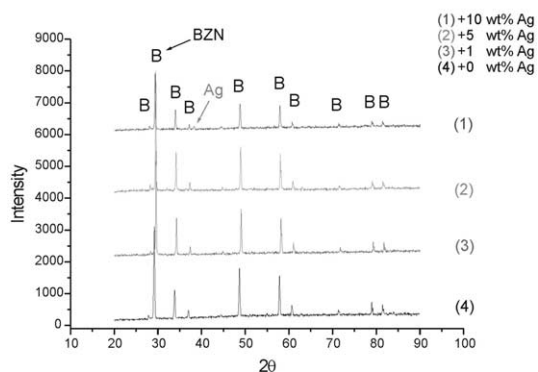


Fig. 3. XRD of BZN-V containing different amount of Ag (0–10 wt%).

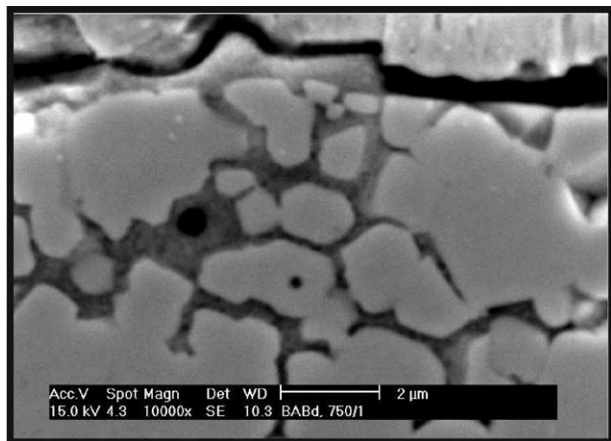


Fig. 4. SEM Photo of BZN-V dense disks cofired with Ag electrode at 850 °C for 1 h shows the formation of channel voids.

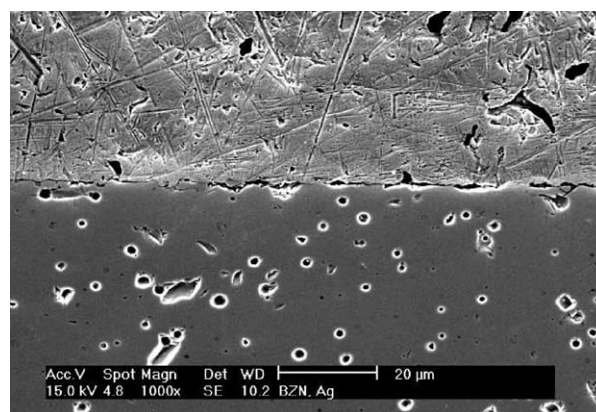


Fig. 5. SEM photo of BZN dense disk cofired with Ag electrode at 850 °C for 1 h shows no formation of channel voids.

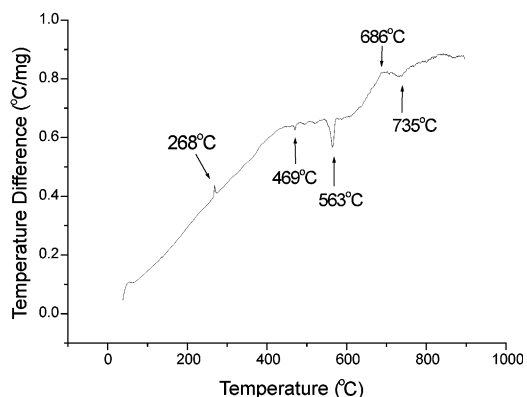


Fig. 6. DTA thermogram of Ag powder mixed with V_2O_5 .

4. Conclusions

BZN-V has been prepared by solid mixing method. The cubic pyrochlore phase of $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ was observed with V-rich phase at the grain boundaries and some Zn-rich phase in the grains. The dielectric relaxation of BZN-V was observed between 40 and 450 K that might be responsible for the low quality factor of the sample. The BZN phase of BZN-V was stable, not reacting with silver. However, silver migration was observed when the BZN-V was cofired with a silver electrode. The result was due to the eutectic reaction between Ag and V_2O_5 .

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