

Silver cofirability differences between $\text{Bi}_{1.5}\text{Zn}_{0.92}\text{Nb}_{1.5}\text{O}_{6.92}$ and $\text{Zn}_3\text{Nb}_2\text{O}_8$

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Abstract

We have investigated systematically the differences of silver cofirability and microwave dielectric properties between $\text{Zn}_3\text{Nb}_2\text{O}_8$ and $\text{Bi}_{1.5}\text{Zn}_{0.92}\text{Nb}_{1.5}\text{O}_{6.92}$ (BZN). Two type dopants: $0.29\text{BaCO}_3\text{--}0.71\text{CuO}$ (BC) and $0.81\text{MoO}_3\text{--}0.19\text{CuO}$ (MC) were used in $\text{Zn}_3\text{Nb}_2\text{O}_8$ and $\text{Bi}_{1.5}\text{Zn}_{0.92}\text{Nb}_{1.5}\text{O}_{6.92}$ ceramics so they can be cofired with silver. The BC-doped ceramics in general have better dielectric properties than those of MC-doped ceramics. The BC-doped $\text{Zn}_3\text{Nb}_2\text{O}_8$ exhibits better dielectric properties than those of BC-doped BZN ($k=14.7$, $Q \times f=8200$ GHz versus $k=120.1$, $Q \times f=1050$ GHz). For silver compatibility study, the interfacial behaviors between microwave dielectric materials and silver were investigated by using X-ray diffractometer, scanning electronic microscope, and electronic probe microanalyzer. No new crystalline phase and no silver migration behavior were found in the BC-doped $\text{Zn}_3\text{Nb}_2\text{O}_8$ ceramics cofired with silver, but slight silver migration was detected for BC-doped BZN. But slight silver migration was detected for MC-doped $\text{Zn}_3\text{Nb}_2\text{O}_8$ and BZN ceramics cofired with silver. Therefore, the good overall properties of BC-doped $\text{Zn}_3\text{Nb}_2\text{O}_8$ are suitable for microwave applications.

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1. Introduction

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. 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 components 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 Ag–Pd electrode with the better properties and lower cost of silver electrodes. However, the melting temperature of silver is low (961°C). A low sintering temperature material is required to cofire with the silver.

Recently, $\text{Zn}_3\text{Nb}_2\text{O}_8$ has emerged as a good microwave material because it exhibits high quality factor.^{1–4} The sintering temperature can be further decreased to 850°C by adding 2 mol% V_2O_5 to $\text{Zn}_3\text{Nb}_2\text{O}_8$, but silver migration behaviors were found after firing the mixture of V_2O_5 -doped $\text{Zn}_3\text{Nb}_2\text{O}_8$ and sil-

ver powder.⁴ $\text{Bi}_2\text{O}_3\text{--ZnO--Nb}_2\text{O}_5$ system has also emerged as a good low sintering ($\sim 1000^\circ\text{C}$) microwave material because it exhibits high dielectric constant and low temperature coefficient of resonance frequency (τ_f).^{5–12} The sintering temperature can also be further decreased to 850°C by adding 2 mol% V_2O_5 to $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$.^{12,13} The silver reacted toward V_2O_5 has also been found.^{13–15} Therefore, there is a need for an alternative sintering aid for Zn–Nb-based microwave material.

Copper oxide has been known as a good sintering aid and less reactive toward silver.^{16,17} Therefore, two eutectic compounds of CuO , $0.81\text{MoO}_3\text{--}0.19\text{CuO}$ ¹⁸ and $0.29\text{BaCO}_3\text{--}0.71\text{CuO}$ ¹⁹ were studied as a sintering aid, respectively, to lower the sintering temperature of $\text{Zn}_3\text{Nb}_2\text{O}_8$ and $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$. We also investigated the interfacial behaviors between the doped ceramics ($\text{Zn}_3\text{Nb}_2\text{O}_8$ and $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$) and silver to determine whether the CuO -based additives for ceramics can be cofired with silver. X-ray diffractometer, scanning electron microscopy, and electronic probe microanalyzer were used to evaluate the extent of silver migration. The results are reported here.

2. Experimental

Reagent grade oxide powders with an appropriate molar ratio of ZnO , and Nb_2O_5 (99.9% purity each, Alfa Chemicals, USA) were used for preparing $\text{Zn}_3\text{Nb}_2\text{O}_8$ by conventional mixed

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solid method. The samples were calcined at 1100 °C for 4 h. Reagent grade oxide powders with an appropriate molar ratio of Bi₂O₃, ZnO, and Nb₂O₅ (99.9% purity each, Alfa Chemicals, USA) were used for preparing Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92} (BZN) samples by conventional mixed solid method. The crystalline phases of calcined Zn₃Nb₂O₈ and BZN powders were confirmed according to the literature data.^{4,12} The two series of powders were characterized by light scattering (Mastersizer 2000, Malvern Instruments, UK) for particle size, B.E.T for surface area (Micromeritics, ASAP2000 BET, USA), electronic probe microanalyzer (EPMA, Joel, JXA-8600SX, Japan) equipped with WDS for chemical composition, and X-ray diffractometer (XRD, PW 1830, Philips, The Netherlands) for the crystalline structure.

Two kinds of CuO-based additives: 0.81MoO₃–0.19CuO and 0.29BaCO₃–0.71CuO were used in our experiments. They were prepared by conventional powder processing. After the crystalline phases of calcined two series of powders were confirmed via the literature data, various amounts of CuO-based additives were added as sintering aid. The two series of powders were pressed under 500 kg/cm² to form tablets (10 mm diameter), and sintered at different temperature for 4 h.

The dielectric properties of sintered Zn₃Nb₂O₈ series tablets were evaluated by network analyzer (Hewlett Packard, 8722ES Network Analyzer, USA).

For the silver migration study, samples were prepared by printing silver electrode over dense tablets then cofired the samples at various temperatures for 4 h. The diffusion distance and concentration of silver were determined by electronic probe microanalyzer (EPMA). The microstructures of sintered samples were evaluated by scanning electron microscopy (SEM) equipped with EDS (Philips, XL-30, The Netherlands).

3. Results and discussion

The Zn₃Nb₂O₈ and Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92} (BZN) have been prepared by using the solid mixing method. The Zn₃Nb₂O₈ powder was calcined at 1100 °C for 4 h, and the calcined Zn₃Nb₂O₈ powder was investigated with XRD. As shown in Fig. 1(a), a pure single phase of Zn₃Nb₂O₈ was formed when the powder was sintered at 1100 °C. The BZN powder was calcined at 900 °C for 2 h, and the calcined powder also showed a pure single phase of BZN as shown in Fig. 1(b). The chemical composition of calcined Zn₃Nb₂O₈ and BZN powder was analyzed by EPMA–WDS. The amount of Zn and Nb remained the same before and after calcination. The amount of bismuth of BZN powder is slightly reduced after calcination at 900 °C for 2 h. This might be due to the volatilization of bismuth. Also the stable cubic pyrochlore phase is preserved as shown in its XRD spectrum.

The two series of ceramics (Zn₃Nb₂O₈ and Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}) with various doping levels of BaCO₃–CuO (BC) or MoO₃–CuO (MC) dopants were sintered at different temperatures for 4 h. The theoretical density of Zn₃Nb₂O₈⁴ is 5.818 g/cm³ and the theoretical density of Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}^{10,13,20} is 7.111 g/cm³. The theoretical density of Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92} powder was measured by

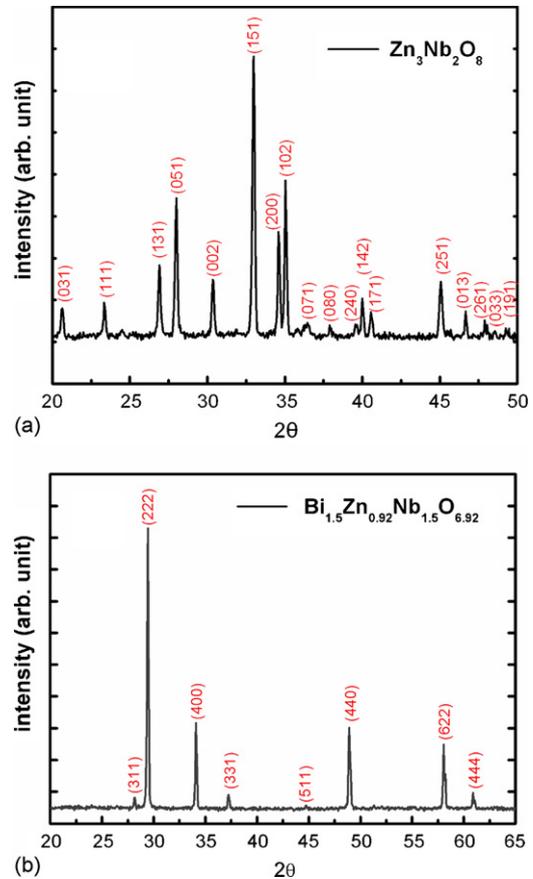


Fig. 1. (a) XRD pattern of Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92} powders calcined at 900 °C for 2 h. (b) XRD pattern of Zn₃Nb₂O₈ powders calcined at 1100 °C for 4 h.

Pycnometer (Quanta Chrome, Ultrapycnometer 1000). Both dopants with a concentration of 3.0 wt.% provide the highest densification of ceramics. Their sintering behaviors are shown in Fig. 2. The eutectic temperature of MoO₃–CuO dopant (710 °C) is lower than that of BaCO₃–CuO dopant (890 °C). Thus, the highest densification process occurred at a lower temperature for MC-doped ceramics due to a liquid phase sintering. The density of BZN series is higher than Zn₃Nb₂O₈ series due to the existence of bismuth. The BZN series exhibits a lower sintering

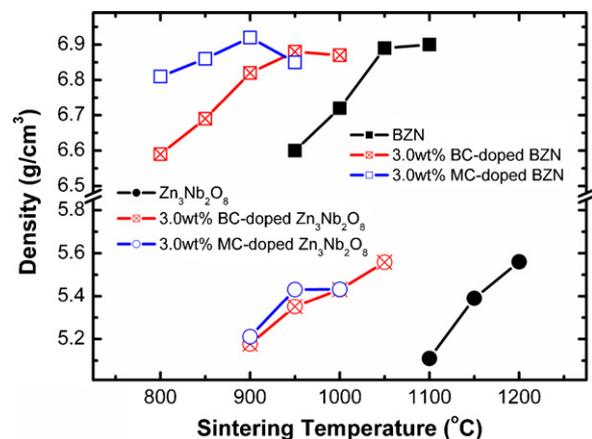


Fig. 2. Densities of Zn₃Nb₂O₈ and Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92} systems sintered at different temperature for 4 h.

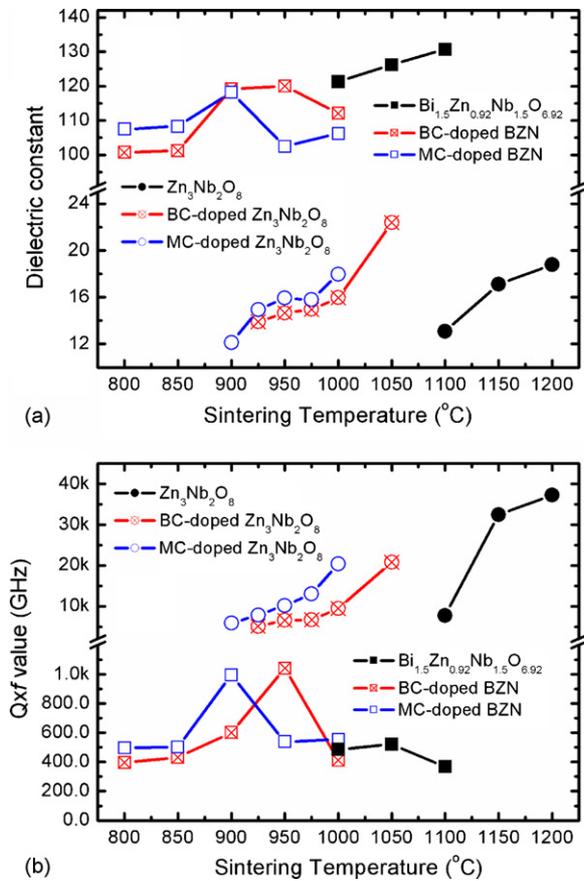


Fig. 3. Microwave dielectric properties of $Zn_3Nb_2O_8$ and $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ systems sintered at different temperature for 4 h: (a) dielectric constant and (b) $Q \times f$ value.

temperature and a higher densification than those of $Zn_3Nb_2O_8$ series.

The optimal dopant (MC or BC) concentration has been found to be 3.0 wt.% for both $Zn_3Nb_2O_8$ and BZN. When the dopant concentration more than 3.0 wt.%, the XRD results revealed the presence of $BaCO_3$ phase for BC dopant and MoO_3 phase for MC dopant that degraded the quality factor of both ceramics. Their microwave dielectric properties were studied for samples sintered at different temperature for 4 h and shown in Fig. 3. The microwave dielectric properties of 3.0 wt.% BC-doped $Zn_3Nb_2O_8$ ceramics are improved with increasing sintering temperature. When the 3.0 wt.% BC-doped $Zn_3Nb_2O_8$ was sintered at 950 °C, its $Q \times f$ value can be reached to 8200 GHz. However, the dielectric constant is only 14.7. When the BC-doped $Zn_3Nb_2O_8$ was sintered at 1050 °C, its $Q \times f$ value can be increased to 21,000 GHz, and the dielectric constant becomes 22.6. The improved dielectric properties at higher sintering temperature are expected due to the increased densities of ceramics ($D_{relative} = 92.1\%$ at 950 °C; $D_{relative} = 96.1\%$ at 1050 °C). The 3.0 wt.% MC-doped $Zn_3Nb_2O_8$ was sintered at 950 °C, its $Q \times f$ value can be reached to 10,200 GHz; however, the dielectric constant is only 15.9. When the MC-doped $Zn_3Nb_2O_8$ was sintered at 1000 °C, its $Q \times f$ value can be increased to 20,400 GHz, and the dielectric constant becomes 18.0. The improvements of dielectric properties are also due to the increasing of den-

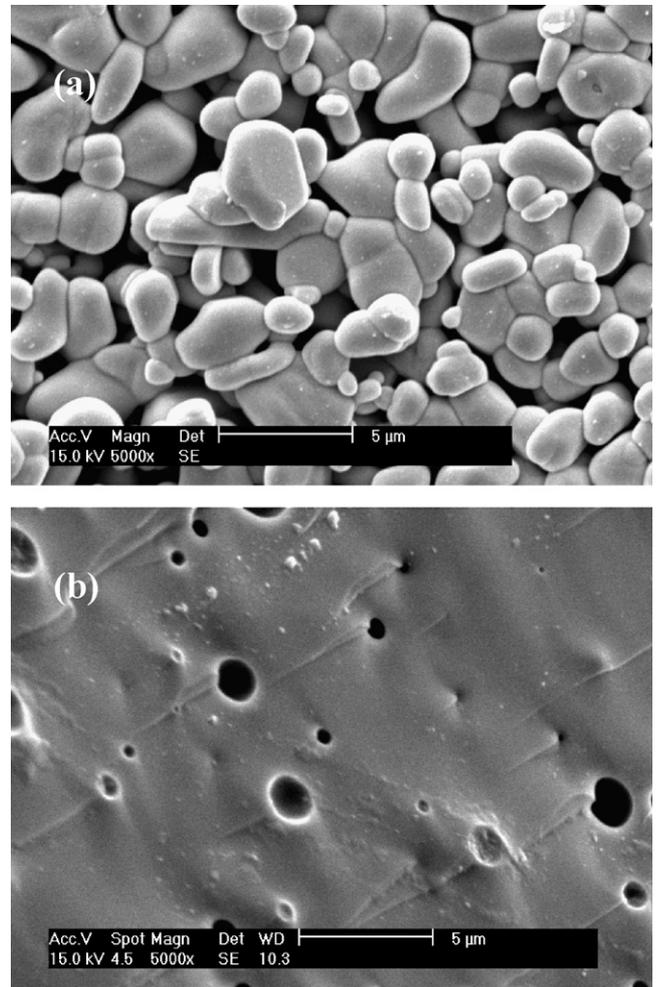


Fig. 4. SEM surface structures of (a) 3.0 wt.% BC-doped $Zn_3Nb_2O_8$ and (b) 3.0 wt.% BC-doped $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ sintered at 950 °C for 4 h.

sity at higher sintering temperature ($D_{relative} = 93.5\%$ at 950 °C; $D_{relative} = 95.1\%$ at 1000 °C). The microwave dielectric properties of MC-doped $Zn_3Nb_2O_8$ ceramics was increased with sintering temperature. The pure BZN cannot be densified below 1050 °C. When 3.0 wt.% BC-doped BZN was sintered at 950 °C, its microwave dielectric constant can be reached to 120.0 at 2.30 GHz, and the $Q \times f$ value is 1050 GHz. The microwave dielectric constant of MC-doped BZN sintered at 900 °C can be reached to 118.2, and the $Q \times f$ value is 1000 GHz.

In order for the ceramics to be cofired with silver, doped samples were sintered at 950 °C for 4 h. The dielectric constant of 3.0 wt.% BC-doped $Zn_3Nb_2O_8$ is much lower than that of 3.0 wt.% BC-doped BZN. The asymmetric structure of BZN results in the higher polarization that exhibits higher dielectric constant. As for the low $Q \times f$ value of the 3.0 wt.% BC-doped BZN, it is due to the effect of dielectric relaxation²⁰ and the presence of voids in this sample (Fig. 4(b)).

The silver migration of two series ceramics cofired with silver electrodes was studied by EPMA and XRD. The extend of silver migration is expressed by the Ag diffusion length measured by EPMA. As shown in Table 1, there are no silver migrations in pure $Zn_3Nb_2O_8$ and BC-doped $Zn_3Nb_2O_8$ ceramics.

Table 1
Physical properties and Ag diffusion distance of $Zn_3Nb_2O_8$ and $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ series ceramics after sintering

Material	Sintering condition	f (GHz)	k	$Q \times f$ (GHz)	Relative density (%)	Ag diffusion length (μm)
$Zn_3Nb_2O_8$	1150 °C, 4 h	7.80	17.1	32,500	92.8	0
3.0 wt.% BC-doped $Zn_3Nb_2O_8$	950 °C, 4 h	8.30	14.7	8,200	92.2	0
3.0 wt.% MC-doped $Zn_3Nb_2O_8$	950 °C, 4 h	8.20	15.9	10,200	93.6	6
$Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$	1050 °C, 4 h	2.40	126.2	550	97.0	10
$Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$	850 °C, 4 h	–	–	–	90.3	0
3.0 wt.% BC-doped $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$	950 °C, 4 h	2.30	120.1	1,050	96.2	25
3.0 wt.% MC-doped $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$	900 °C, 4 h	2.30	118.2	1,000	96.2	35
0.6 wt.% V_2O_5 -doped $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$	850 °C, 1 h	2.90	148.0	120	97.1	620

However, the MC-doped $Zn_3Nb_2O_8$ exhibited a silver diffusion distance of 6 μm . For pure BZN ceramics, the silver diffusion length was increased from 0 to 10 μm when the sintering condition was changed from 850 °C for 1 h to 1050 °C for 4 h. We suspect that the slight silver migration was resulted from the reaction between bismuth and silver. A very serious Ag migration (620 μm) was observed for our control sample: 0.6 wt.% V_2O_5 -doped BZN due to the reaction between V_2O_5 and Ag. When the MC-doped BZN was cofired with silver electrode at 950 °C, an active MoO_3 ingredient cause a silver migration. A porous layer containing silver was observed at the interface between ceramics and silver. The existence of the porous layer may be due to the reaction between Ag and other elements, such as Mo, Bi. The silver migration was detected for MC-doped $Zn_3Nb_2O_8$. However, no porous layer was observed near the interface. The silver migration is possible between Ag and MoO_3 because they can form Ag–Mo oxide compounds.^{15,16} We tried to use XRD to confirm the formation of Ag–Mo oxide compounds. However, the concentration was too low to detect.

4. Conclusions

Eutectic compounds 0.81 MoO_3 –0.19 CuO (MC) and 0.29 $BaCO_3$ –0.71 CuO (BC) are good sintering aids for Zn–Nb-based ceramics. For samples sintered at low temperature (~ 950 °C), the BC-doped $Zn_3Nb_2O_8$ exhibits high $Q \times f$ value at 8.3 GHz ($k=14.7$, $Q \times f=8200$ GHz) and BC-doped BZN exhibits high dielectric constant at 2.3 GHz ($k=120$, $Q \times f=1050$ GHz). The low dielectric constant of $Zn_3Nb_2O_8$ is resulted from its poor densification. The low $Q \times f$ value of BZN is resulted from its dielectric relaxation and containing voids. No new crystalline phase and no silver migration behavior were found in BC-doped $Zn_3Nb_2O_8$ ceramics cofired with silver. However, a slight silver migration was observed for BC-doped BZN due to the reaction between Ag and Bi. Thus, $Zn_3Nb_2O_8$ is cofired better with silver than BZN.

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