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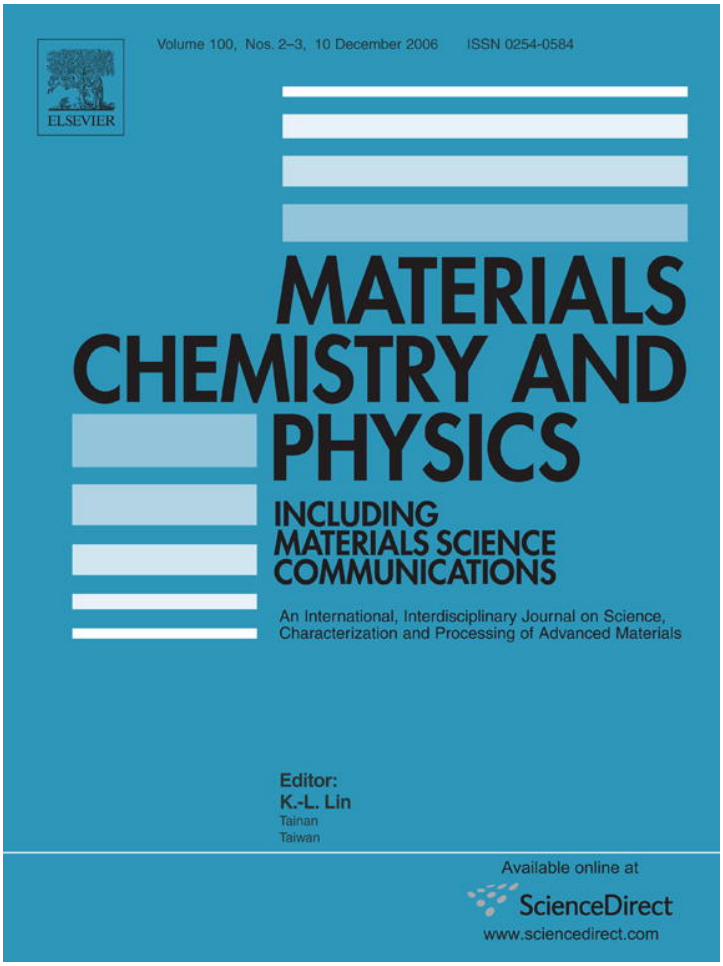

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Silver cofirable $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ microwave ceramics containing CuO-based dopants

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Abstract

Bi_2O_3–ZnO–Nb_2O_5 system has emerged as a good low sintering (∼1050 °C) microwave material because it exhibits high dielectric constant and low temperature coefficient of resonance frequency (τ_f). We have lowered the sintering temperature of $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ (BZN) below 900 °C by using 3 wt.% of CuO-based dopants, such as $0.21BaCO_3$–0.79CuO (BC) and $0.81MoO_3$–0.19CuO (MC). The doped BZN exhibits high microwave dielectric constant at 2.3 GHz ($k \sim 120$). The interfacial behavior between BZN and silver was investigated by using X-ray diffractometer, scanning electronic microscope, and electronic probe microanalyzer. The extent of silver migration of MC and BC dopants is reduced at least by one order of magnitude as compared with V_2O_5 dopant when the samples was prepared at 900 °C for 4 h. Thus, CuO-based dopants can replace V_2O_5 to lower the sintering temperature of BZN and to be cofired with silver.
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Keywords: $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$; Microwave dielectric property; Low sintering temperature; Silver migration; Cofired

1. Introduction

Most conventional ceramics that have excellent microwave dielectric properties such as BMT ($BaMg_{1/3}Ta_{2/3}O_3$), BNT ($BaO\text{-}Nd_2O_3\text{–}TiO_2$), 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, Bi_2O_3–ZnO–Nb_2O_5 system has emerged as a good low sintering (∼1000 °C) microwave material because it exhibits high dielectric constant and low temperature coefficient of resonance frequency (τ_f) [1–6]. The sintering temperature can be further decreased to 850 °C by adding 2 mol% V_2O_5 to $Bi_{1.5}ZnNb_{1.5}O_7$ [7–9]. However, the silver has found to be reactive toward V_2O_5 [9,10].

Copper oxide has been known as a good sintering aid and less reactive toward silver [11,12]. We studied two CuO-based eutectic compounds: $0.81MoO_3$–0.19CuO [13] and $0.29BaCO_3$–0.71CuO [14] as sintering aid to lower the sintering temperature of BZN. We also investigated the interfacial behavior between the doped BZN and silver to determine any silver migration problem. The BZN with a composition of $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ was used in the study instead of $Bi_{1.5}ZnNb_{1.5}O_7$, because the former has better quality factor [15,16].

2. Experimental

Reagent grade oxide powders with an appropriated molar ratio of Bi_2O_3, ZnO, and Nb_2O_5 (99.9% purity each, Alfa Chemicals, USA) were used to prepare $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ (BZN) samples using the conventional mixed solid method. The samples were calcined at 900 °C for 2 h. For lowering the sintering temperature study, two kinds of CuO-based dopants, i.e., MoO_3–CuO (MC) and $BaCO_3$–CuO (BC) were used in our experiments. The selected $0.81MoO_3$–0.19CuO and $0.21BaCO_3$–0.79CuO compositions were prepared by conventional powder processing. After the crystalline phases of calcined BZN powder samples were confirmed according to the literature data [9]. Then, the CuO-based dopants were added as sintering aids.

The BZN-based ceramic powders were characterized by light scattering (Mastersizer 3000, Malvern Instruments, UK) for particle size, BET for surface area (Micromeritics, ASAP2000 BET, USA), inductively coupled plasma-mass spectrometer (ICP-Mass, Sciex Elan 5000, Perkin Elmer, USA) and electronic

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probe micro-analyzer (EPMA, Joel, JXA-8600SX, Japan) for chemical composition, and X-ray diffractometer (XRD, PW 1830, Philips, Nederland) for the crystalline structure. The BZN series powders were pressed at 500 kg cm^{-2} to form tablets (8 mm diameter), and sintered at different temperature for 4 h. The dielectric properties of sintered 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 BZN-based ceramic tablets and cofiring the products at various temperatures for 4 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 electron microscopy (SEM) equipped with EDS (Philips, XL-30, Netherlands).

3. Results and discussion

The $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ has been prepared by the solid mixing method. The surface area and particle size of the BZN powder were 6.98 m^2 g^{-1}, 0.68 μm, respectively, measured by light scattering and BET.

The chemical compositions of the calcined powder were analyzed by ICP-Mass and EPMA-WDS, these results were listed in Table 1. The amount of bismuth in both analysis is slightly reduced after calcination at 900 °C for 2 h. This might be due to the volatilization of bismuth. However, the stable cubic pyrochlore phase is preserved as shown in its XRD spectrum (Fig. 1).

BZN ceramics with various doping levels of $BaCO_3$–CuO (BC) or MoO_3–CuO (MC) dopants were sintered at different temperatures for 4 h. The specific surface areas and particle sizes of the different composition of doped BZN powders are summarized in Table 2. Their sintering behaviors are shown in Fig. 2. Both dopants with a concentration of 3.0 wt.% provide the highest densification of BZN. The eutectic temperature of MoO_3–CuO dopant (710 °C) is lower than that of $BaCO_3$–CuO dopant (890 °C). Thus, the highest densification process occurred at a lower temperature for MC doped BZN ceramics (900 °C versus 950 °C) due to a liquid phase sintering.

The BZN samples exhibit cubic pyrochlore phase were studied further for their microwave dielectric properties. The results are plotted in Fig. 3. 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 quality factor is 1050 GHz. The microwave dielectric constant of MC doped BZN sintered at 900 °C can be reached to 118.2, and the quality factor is 1000 GHz. The

Table 1
Molar ratio of $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ measured by ICP-mass spectrometry and EPMA

Samples		Bi	Zn	Nb
Before calcine		1.50	0.92	1.50
After calcine at 900 °C for 1 h	ICP-mass	1.32	0.92	1.50
	EPMA	1.35	0.92	1.50

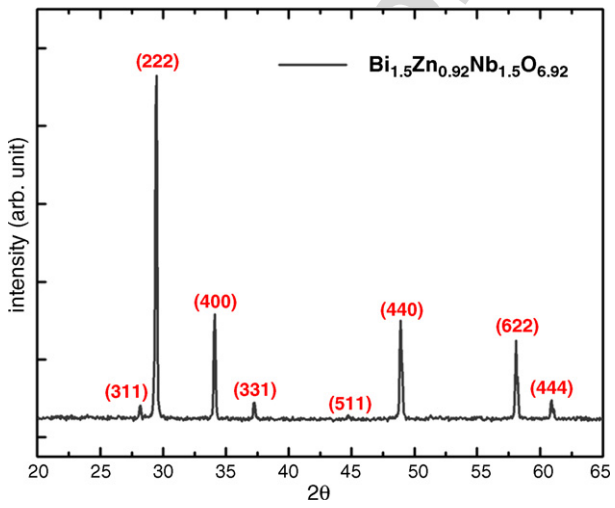

Fig. 1. XRD pattern of $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ powder calcined at 900 °C for 2 h.

Table 2
Specific surface area and particle size of $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ series powders

Material	Surface area (m^2/g)	Particle size (μm)
$Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$	6.98	0.68
3.0 wt.% BC doped $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$	8.89	0.63
3.0 wt.% MC doped $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$	10.38	0.55

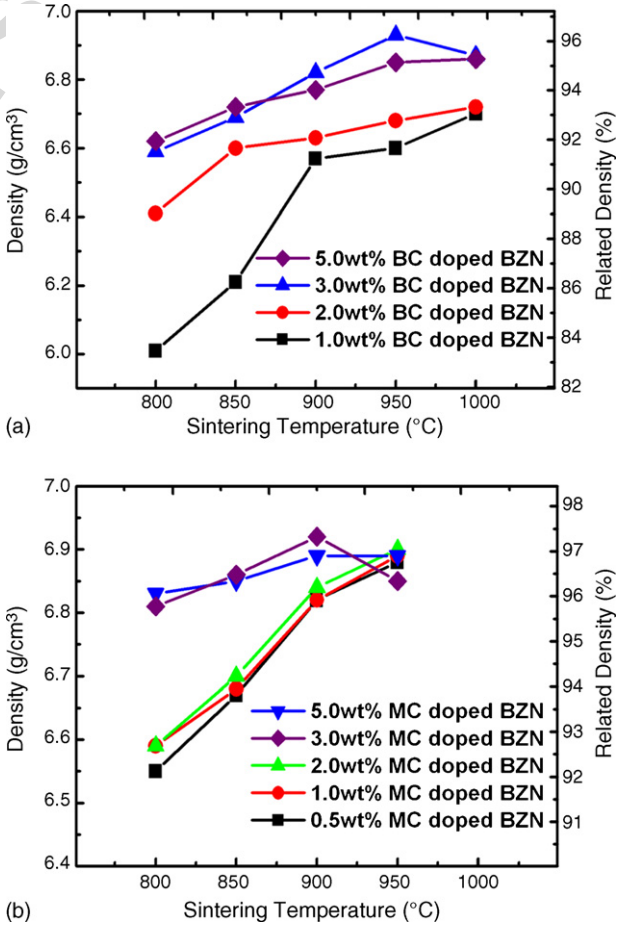

Fig. 2. Densities of (a) BC doped $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ and (b) MC doped $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ sintered at different temperatures for 4 h.

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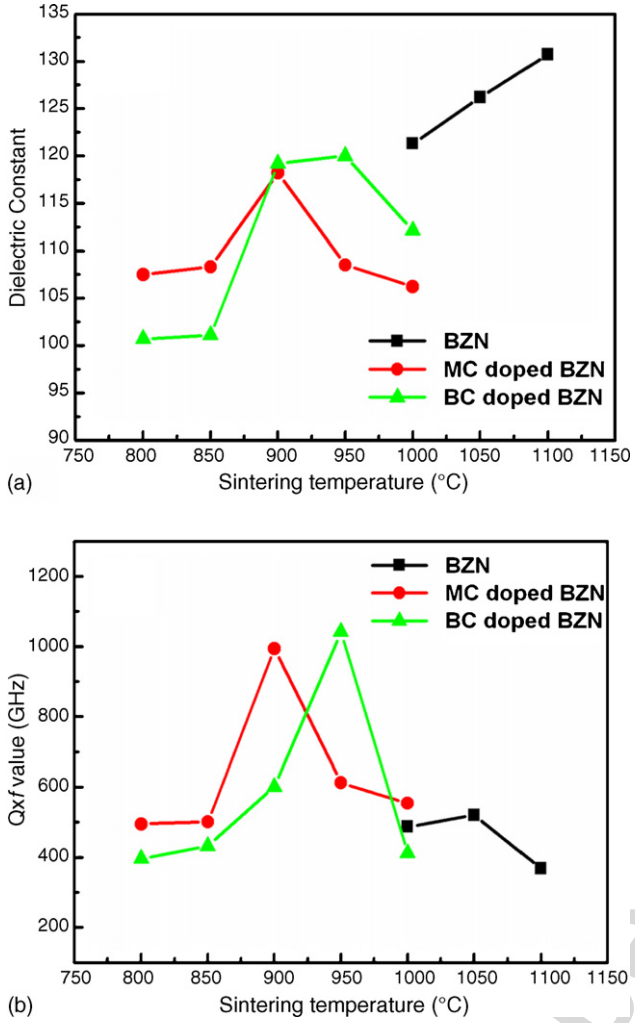

Fig. 3. Microwave dielectric properties of pure $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ and CuO-based doped $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ sintered at different temperatures for 4 h. (a) Dielectric constant; (b) $Q \times f$ value.

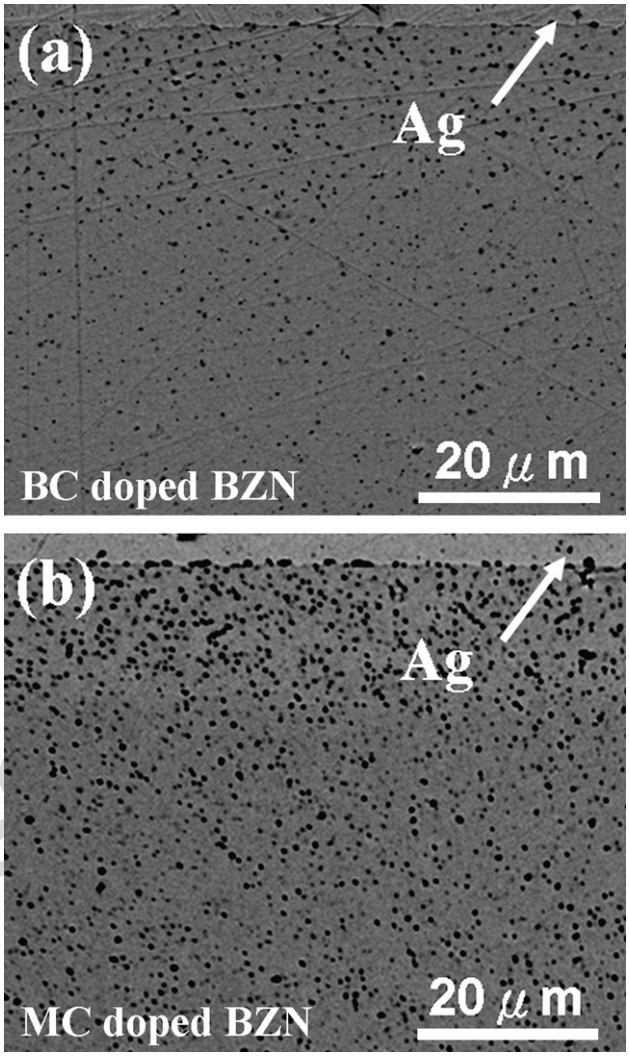

Fig. 4. SEM photos of (a) BC doped $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ dense tablet cofired with Ag at 950 °C for 4 h and (b) MC doped $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ dense tablet cofired with Ag at 900 °C for 4 h.

relative low quality factor Q of BZN ceramics results from the dielectric relaxation and voids present in the samples [16].

For silver migration studies, we cofired dense BZN tablets with silver electrode at optimum sintering condition. The migration distance and concentration of silver were determined by electronic probe micro-analyzer (EPMA) equipped with wavelength dispersive spectrometer. The results are listed in Table 3. For pure $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ ceramics, the distance of silver migration was increased from 0 to 10 μm when the sintering condition was increased from 850 °C, 1 h to 1050 °C, 4 h. However, no silver migration was observed for $Zn_3Nb_2O_8$ sintered at 1150 °C for 4 h. We suspected that the slight migration was due to the reaction between bismuth and silver. A serious Ag migration (620 μm) was observed for 0.6 wt.% V_2O_5 doped BZN due to the reaction between V_2O_5 and Ag.

Fig. 4a showed the SEM photo of 3.0 wt.% BC doped BZN cofired with silver at 950 °C for 4 h. A porous layer with a thickness about 30 μm from the interface was observed. The

Table 3
Physical properties and Ag diffusion distance of $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ series ceramics after sintering

Material	Sintering condition	Relative density (%)	f (GHz)	k	$Q \times f$ (GHz)	Ag diffusion distance (μm)
$Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$	850 °C, 1 h	90.3	–	–	–	0
$Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$	1050 °C, 4 h	97.0	2.40	126.2	520	10
$Zn_3Nb_2O_8$	1150 °C, 4 h	92.7	7.80	17.1	32500	0
0.6 wt.% V_2O_5 doped $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$	850 °C, 1 h	97.1	2.90	148.0	118	620
3.0 wt.% BC doped $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$	950 °C, 4 h	96.2	2.30	120.1	1050	25
3.0 wt.% MC doped $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$	900 °C, 4 h	96.2	2.30	118.2	1000	35

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BC doped BZN exhibited a silver migration with an average distance of 25 μm measured by EPMA-WDS. Fig. 4b showed the SEM photo of 3.0 wt.% MC doped BZN dense tablets cofired with silver at 900 °C for 4 h. A porous layer was also observed about 50 μm away from the interface. Its average silver migration distance was 35 μm from EPMA-WDA. The existence of the porous layer may be due to the reaction between Ag and other elements. The reaction between Ag and Bi; Ag and Mo to form compounds are known. However, we cannot detect them by XRD due to their low concentration.

4. Conclusions

Eutectic compounds $0.81MoO_3$–$0.19CuO$ (MC) and $0.21BaCO_3$–$0.79CuO$ (BC) are good sintering aids for $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$. At 3.0 wt.% level, the sintering temperature can be reduced from 1050 to 900 °C. The doped BZN exhibits high dielectric constant (∼120 at 2.30 GHz). The extent of silver migration of MC and BC dopants is reduced at least by one order of magnitude as compound with V_2O_5 dopant. Thus MC and BC doped BZN are suitable to be cofired with silver.

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