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Microwave dielectric properties of doped $Zn_3Nb_2O_8$ ceramics sintered below 950 °C and their compatibility with silver electrode

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Abstract

$Zn_3Nb_2O_8$ has been considered as candidate microwave materials due to its high quality factor. However, $Zn_3Nb_2O_8$ has to be sintered above 1200 °C. We have lowered $Zn_3Nb_2O_8$ sintering temperature to 950 °C by using 3 wt.% of BC additives ($0.29BaCO_3$–$0.71CuO$). The doped $Zn_3Nb_2O_8$ exhibits good microwave properties at 8.3 GHz ($k = 14.7$, $Q \times f = 8200$ GHz). The interfacial behavior between $Zn_3Nb_2O_8$ dielectric and silver was investigated by using X-ray diffractometer, scanning electronic microscope, and electronic probe microanalyzer. No new crystalline phase and no silver migration behavior were found after cofiring doped $Zn_3Nb_2O_8$ and silver electrode at 950 °C for 4 h. The low sintering temperature BC doped $Zn_3Nb_2O_8$ with high $Q \times f$ value has a potential for microwave applications.

Keywords: $Zn_3Nb_2O_8$; Microwave materials; Dielectric properties; Diffusion; Silver; Powders solid state reaction

1. Introduction

Most conventional ceramics that have excellent microwave dielectric properties such as BMT ($BaMg_{1/3}Ta_{2/3}O_3$), BNT (BaO–Nd_2O_3–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, $Zn_3Nb_2O_8$ has emerged as a good microwave material because it exhibits high quality factor [1–5]. The sintering temperature can be further decreased to 850 °C by adding 2 mol% V_2O_5 to $Zn_3Nb_2O_8$, but silver migration behavior was found after firing the mixture of V_2O_5 doped $Zn_3Nb_2O_8$ and silver powder.

Copper oxide has been known as a good sintering aid and less reactive toward silver [5–9]. Therefore, we studied two eutectic compounds of CuO, $0.81MoO_3$–$0.19CuO$ [10] and $0.29BaCO_3$–$0.71CuO$ [11] as sintering aid to lower the sintering temperature of $Zn_3Nb_2O_8$. We also investigated the interfacial behavior between the doped $Zn_3Nb_2O_8$ and silver to determine whether the CuO-based additives for $Zn_3Nb_2O_8$ can be cofired with silver. X-ray diffractometer, scanning electron microscope, and electronic probe micro-analyzer were used to evaluate the extent of silver migration. The results are reported here.

2. Experimental

Reagent grade oxide powders with an appropriated molar ratio of ZnO, and Nb_2O_5 (99.9% purity each, Alfa Chemicals, USA) were used to prepare $Zn_3Nb_2O_8$ using the conventional mixed solid method. The samples were calcined at 1100 °C for 2 h. Two kinds of CuO-based additives: $0.81MoO_3$–$0.19CuO$ and $0.21BaCO_3$–$0.79CuO$ were used in our experiments. They were prepared by conventional powder processing. After the crystalline phases of calcined $Zn_3Nb_2O_8$ powder were confirmed via the literature data [1], various amount of CuO-based additives were added as sintering aid.

The $Zn_3Nb_2O_8$ series powders were characterized by light scattering (Mastersizer 2000, Malvern Instruments, UK) for particle size, BET for specific 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, The Netherlands) for the crystalline structure. The $Zn_3Nb_2O_8$ series powders were pressed at $5 \times 10^6\ kg\,m^{-2}$ to form tablets (8 mm diameter), and sintered at different temperature for 4 h.

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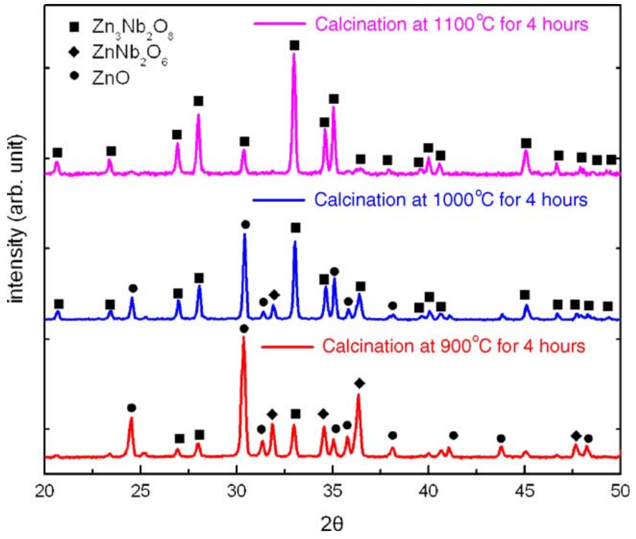

Fig. 1. XRD patterns of $Zn_3Nb_2O_8$ powders calcined at different temperatures for 4 h.

The dielectric properties of sintered $Zn_3Nb_2O_8$ 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 $Zn_3Nb_2O_8$ series 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) equipped with wavelength dispersive spectrometer. The microstructures of sintered samples were evaluated by scanning electron microscopy (SEM) equipped with energy dispersive spectrometer (Philips, XL-30, The Netherlands).

3. Results and discussion

The $Zn_3Nb_2O_8$ has been prepared by the solid mixing method. The $Zn_3Nb_2O_8$ powder was calcined at 900, 1000 and 1100 °C, respectively. The calcined $Zn_3Nb_2O_8$ powders were investigated with XRD. As shown in Fig. 1, a pure single phase of $Zn_3Nb_2O_8$ was formed when the powder was sintered at 1100 °C. At 900 °C, a phase of $ZnNb_2O_6$ containing ZnO was formed. At 1000 °C, a major phase of $ZnNb_2O_6$ combined with a secondary phase of $Zn_3Nb_2O_8$ was found. The existence of secondary phase or other component degraded the dielectric

Table 1
Specific surface area and particle size of $Zn_3Nb_2O_8$ series powders

Material	Surface area ($m^2\ g^{-1}$)	Particle size (μm)
$Zn_3Nb_2O_8$	3.33	0.89
3.0 wt.% BC doped $Zn_3Nb_2O_8$	3.37	0.87
3.0 wt.% MC doped $Zn_3Nb_2O_8$	3.87	0.82

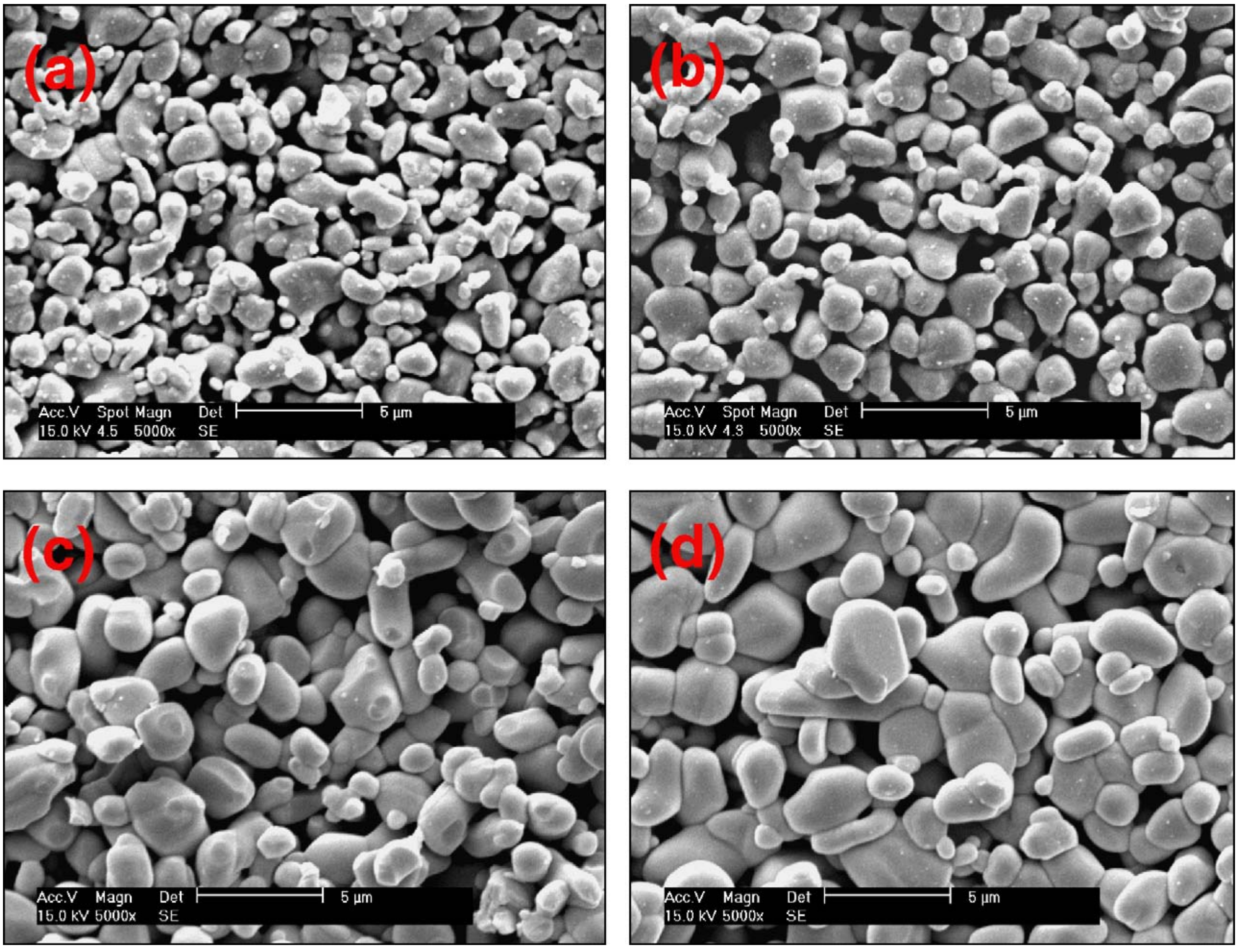

Fig. 2. SEM surface structures of BC doped $Zn_3Nb_2O_8$ at (a) 1.0 wt.% (b) 3.0 wt.% and MC doped $Zn_3Nb_2O_8$ at (c) 1.0 wt.% (d) 3.0 wt.% at 950 °C for 4 h.

Table 2
Molar ratio of $Zn_3Nb_2O_8$ series ceramics measured by EPMA

Material	Sintering condition	Molar ratio of $Zn_3Nb_2O_8$ series ceramics sintered at 950 °C				
		Zn	Nb	Cu	Ba	Mo
$Zn_3Nb_2O_8$	1150 °C, 4 h	3.0	2.0	–	–	–
3.0 wt.% BC doped $Zn_3Nb_2O_8$	950 °C, 4 h	3.0	2.0	0.01	0.03	–
3.0 wt.% MC doped $Zn_3Nb_2O_8$	950 °C, 4 h	3.0	2.0	0.01	–	0.02

properties of $Zn_3Nb_2O_8$; therefore, all $Zn_3Nb_2O_8$ powders were calcined at 1100 °C.

The chemical composition of calcined $Zn_3Nb_2O_8$ powder was analyzed by ICP-Mass and EPMA equipped with wavelength dispersive spectrometer. The amount of Zn and Nb remained the same before and after calcination. The specific surface area and particle size of the $Zn_3Nb_2O_8$ series powders are shown in Table 1.

The BC doped $Zn_3Nb_2O_8$ and MC doped $Zn_3Nb_2O_8$ ceramics were sintered at 950 °C for 4 h. Table 2 shows the chemical compositions of doped $Zn_3Nb_2O_8$ ceramics after sintering at 950 °C, which are the same as before sintering. Thus, the doped $Zn_3Nb_2O_8$ ceramics exhibit good composition stability. The choice of 950 °C sintering temperature is for the purpose of cofiring ceramics with silver. Fig. 2 shows the SEM photos of sintered BC doped and MC doped $Zn_3Nb_2O_8$. The grain size of BC doped and MC doped $Zn_3Nb_2O_8$ increases with the amounts of additives. The grain size of MC doped $Zn_3Nb_2O_8$ is larger than that of BC doped $Zn_3Nb_2O_8$. The eutectic temperature (710 °C) of MoO_3–CuO additive is lower than that of $BaCO_3$–CuO additive (890 °C). Thus, the liquid phase sintering process occurred at a lower temperature for MC doped $Zn_3Nb_2O_8$ ceramics.

The BC doped $Zn_3Nb_2O_8$ ceramics were sintered from 925 to 1050 °C for 4 h. Their dielectric properties are shown in Fig. 3. The microwave dielectric properties of BC doped $Zn_3Nb_2O_8$ ceramics are improved with increasing sintering temperature. However, their quality factor degraded when the amount of BC additives was more than 3.0 wt.%. Their XRD patterns indicate that the degradation was due to the existence of secondary phase ($BaCO_3$). When the 3.0 wt.% BC doped $Zn_3Nb_2O_8$ was sintered at 950 °C, its quality factor can be reached to 8,200 GHz. However, the dielectric constant is only 14.7. When the BC doped $Zn_3Nb_2O_8$ was sintered at 1050 °C, its quality factor 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 ($D_{\text{relative}} = 92.1\%$ at 950 °C; $D_{\text{relative}} = 96.1\%$ at 1050 °C).

The MC doped $Zn_3Nb_2O_8$ was sintered from 925 to 1000 °C for 4 h. As shown in Fig. 4, when the 3.0 wt.% MC doped $Zn_3Nb_2O_8$ was sintered at 950 °C, its quality factor 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 quality factor 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 density at higher sintering temperature ($D_{\text{relative}} = 93.5\%$ at 950 °C; $D_{\text{relative}} = 95.1\%$ at 1000 °C). The microwave dielectric properties of MC doped $Zn_3Nb_2O_8$ ceramics was increased with sintering temperature; however, its quality factor degraded when the amount of MC additives was more than 3.0 wt.%. Their XRD patterns indicate that the degradation was due to the presence of secondary phase (MoO_3).

Table 3 summaries the physical properties and dielectric properties of BC doped $Zn_3Nb_2O_8$ and MC doped $Zn_3Nb_2O_8$. At 950 °C silver cofiring sintering temperature, MC doped $Zn_3Nb_2O_8$ exhibited better properties than BC doped $Zn_3Nb_2O_8$. Thus, MC is a better sintering aid than BC to obtain a dense $Zn_3Nb_2O_8$.

For the silver migration study, samples of $Zn_3Nb_2O_8$ ceramics cofired with silver electrodes were analyzed by EPMA and

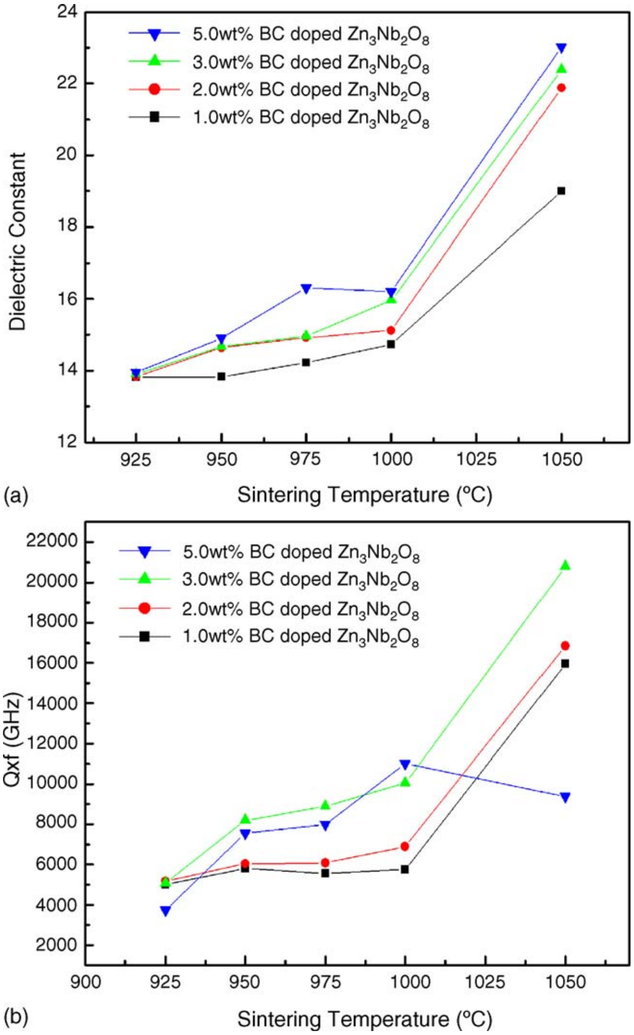

Fig. 3. Microwave dielectric properties of BC doped $Zn_3Nb_2O_8$ ceramics were measured by network analyzer (a) dielectric constant, (b) $Q \times f$ value.

Table 3
Physical properties and Ag diffusion distance of $Zn_3Nb_2O_8$ series ceramics after sintering

Material	Sintering condition	Relative density (%)	f (GHz)	k	$Q \times f$ (GHz)	Ag diffusion distance (μm)
$Zn_3Nb_2O_8$	1150 °C, 4 h	92.7	7.8	17.1	32500	0
3.0 wt.% BC doped $Zn_3Nb_2O_8$	950 °C, 4 h	92.1	8.3	14.7	8200	0
3.0 wt.% MC doped $Zn_3Nb_2O_8$	950 °C, 4 h	93.5	8.2	15.9	10200	6

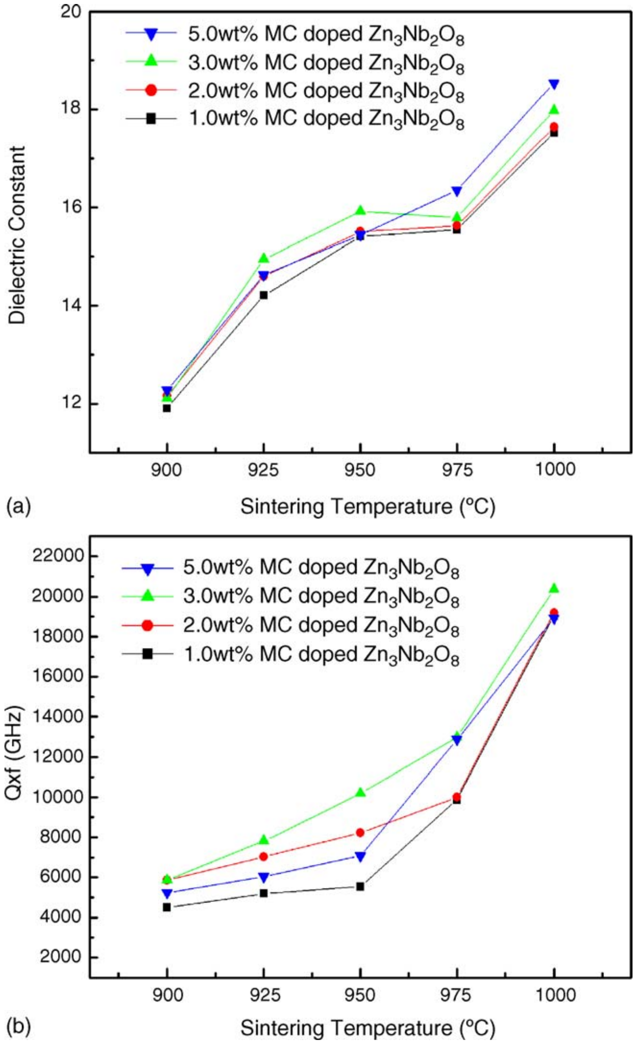

Fig. 4. Microwave dielectric properties of MC doped $Zn_3Nb_2O_8$ ceramics were measured by network analyzer (a) dielectric constant, (b) $Q \times f$ value.

XRD. As shown in Table 3, there are no silver migrations in pure $Zn_3Nb_2O_8$ and BC doped $Zn_3Nb_2O_8$ ceramics. However, the MC doped $Zn_3Nb_2O_8$ exhibited a silver migration with an average distance of 6 μm. The silver migration was possible due to the reaction between Ag and MoO_3 to form Ag–Mo oxide compounds [8,9]. We tried to use XRD to confirm the formation of Ag–Mo oxide compounds. However, the concentration was too low to detect it.

4. Conclusion

Eutectic compounds $0.81MoO_3$–$0.19CuO$ (MC) and $0.21BaCO_3$–$0.79CuO$ (BC) are good sintering aids for $Zn_3Nb_2O_8$. At 3.0 wt.% level, the sintering temperature can be reduced from 1150 to 950 °C. The MC additive is a better sintering aid than BC additive in terms of densification and dielectric properties of $Zn_3Nb_2O_8$. However, an active MoO_3 ingredient causes a silver migration, when the MC doped $Zn_3Nb_2O_8$ was cofired with silver electrode at 950 °C. The BC doped $Zn_3Nb_2O_8$ exhibited good overall properties such as low sintering temperature, inert to silver, and high quality factor ($Q \times f = 8200$ GHz). It has a potential for microwave applications.

Acknowledgments

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References

[1] Y.-C. Lee, C.-H. Lin, I.-N. Lin, Mater. Chem. Phys. 79 (2003) 124.
[2] D.-W. Kim, J.-H. Kim, J.-R. Kim, K.-S. Hong, Jpn. J. Appl. Phys. 40 (2001) 5994.
[3] W.-F. Su, S.-C. Lin, J. Eur. Ceram. Soc. 23 (2003) 2593.
[4] L.B. Kong, J. Ma, H. Huang, R.F. Zhang, T.S. Zhang, J. Alloys Compd. 347 (2002) 308.
[5] D.-W. Kim, K.-H. Ko, K.-S. Hong, J. Am. Ceram. Soc. 84 (2001) 1286.
[6] S.-Y. Chen, Y.-J. Lin, Jpn. J. Appl. Phys. 40 (2001) 3305.
[7] H. Kagata, T. Inoue, J. Kato, Jpn. J. Appl. Phys. 31 (1992) 3152.
[8] E. Wenda, J. Therm. Anal. 36 (1990) 1417.
[9] M. Valant, D. Suvorov, J. Am. Ceram. Soc. 83 (2000) 2721.
[10] R.S. Roth, J.R. Dennis, H.F. McMurdie, Phase Diagrams for Ceramists, VI. American Ceramic Society, Westerville, 1987, p. 6541.
[11] W. Zhang, K. Osamura, S. Ochiai, J. Am. Ceram. Soc. 73 (1990) 1958.