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Microwave Dielectric Properties of Low-Temperature Sintered $Bi_2[Zn_{1/3}(Nb_{1-x}Ta_x)_{2/3}]_2O_7$†

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After $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ (BZN) and $Bi_2(Zn_{1/3}Ta_{2/3})_2O_7$ (BZT) were calcined at 900 ºC and then sintered at 900 ºC, respectively, microwave dielectric properties of BZN were quality factor (Qf_0) = 3,584 GHz, dielectric constant (ε_r)=77 and temperature coefficient of resonant frequency (τ_f) = -34.2 ppm/ºC. Those of BZT were Qf_0 = 3,640 GHz, ε_r = 64 and τ_f = 2.2 ppm/ºC. These two bismuth (Bi) based composition are known to be adequate for microwave application. However BZT has superior $Q{\cdot}f_0$ to BZN, but higher sintering temperature which make BZT difficult for co-firing with Ag electrode, while BZN can be co-fired with Ag electrode, but lower Qf_0 than BZT. Therefore in this study, $Bi_2[Zn_{1/3}(Nb_{1-x}Ta_x)_{2/3}]_2O_7$ (BZNT), solid solution between BZT and BZN, was synthesized and sintered at various temperatures for investigation. As amount of Ta substituting Nb increased, sintered density and $Q{\cdot}f_0$ increased while ε_r decreased. Temperature coefficient of resonant frequency (τ_f) changed from negative to positive region. When BZNT (x = 0.5) was sintered at 900 ºC, dielectric properties were Qf_0 = 4,229 GHz, ε_r = 71 and τ_f = 24.7 ppm/ºC.

Keywords: $Bi_2[Zn_{1/3}(Nb_{1-x}Ta_x)_{2/3}]_2O_7$, High dielectric constant, $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$, $Bi_2(Zn_{1/3}Ta_{2/3})_2O_7$, LTCC.

INTRODUCTION

As info-communicative devices need to process large amount of data in high speed, higher frequency region with broader band needs to be adopted. And with this trend, passive components in mobile communication have been mainly fabricated with dielectric ceramic materials which have superior dielectric properties in microwave (*i.e.*, high frequency) ranges. Especially the low temperature co-fired ceramic (LTCC) technology, which can achieve both the modularization of passive components and the high integrity in substrate at the same time, has been focused out to solve problems such as miniaturization of electronic components in low cost with multi-functionality[1,2].

Microwave dielectric materials need to have high dielectric constant (ε_r) for miniaturization, high quality factor (Qf_0) for high self-resonant frequency (SRF) and lower temperature coefficient (τ_f) near 0 ppm/ºC for stable SRF. Bismuth-based LTCC materials such as $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ (BZN), $Bi_2(Zn_{1/3}Ta_{2/3})_2O_7$ (BZT) are known to have superior dielectric properties. Both have similar sintering behaviour and dielectric properties.

In this study, dielectric properties of BZN and BZT in microwave range were examined and then phase variation of $Bi_2[Zn_{1/3}(Nb_{1-x}Ta_x)_{2/3}]_2O_7$ (BZNT) with calcination temperature was investigated. Sintering behaviour, microstructures and dielectric properties of BZNT with tantalum (Ta) amount was analyzed. Diffusion state at interface between BZNT and silver (Ag) electrode was studied when both were co-fired.

EXPERIMENTAL

Using Bi_2O_3, ZnO, Nb_2O_5, Ta_2O_5 of high purity (> 99.0 %), BZT, BZN and BZNT was prepared by common oxide solid state synthesis. Each raw material powder was weighed for $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$, $Bi_2(Zn_{1/3}Ta_{2/3})_2O_7$ and $Bi_2[Zn_{1/3}(Nb_{1-x}Ta_x)_{2/3}]_2O_7$ (x = 0.0, 0.2, 0.5, 0.7, 1.0), respectively and then mixed by ball milling in ethanol with yttria-stabilized zirconia (YSZ) media for 24 h. Mixed powder was dried at 100 ºC for 24 h. Each dried powder was calcined at 800 and 900 ºC for 2 h. Calcined powders were wet-milled for 24 h and then dried for 24 h. Prepared powders were formed into specimens of 103 diameter by uni-axial pressing with pressure of 1 kg/cm^2. Formed specimens were sintered at 800, 900 and 1,000 ºC for 2 h with heating rate of 5 ºC/min. Sintered specimens were cooled naturally in kiln. Phase variation of prepared specimens was evaluated by X-ray diffractometer (XRD, Rint-2000, Rigaku, Japan). Microstructures of thermally etched specimens

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were observed by field-emission scanning electron microscope (FE-SEM; JSM-6700F, Jeol, Tokyo, Japan). Probable reaction or diffusion between Ag and ceramic body was examined by energy dispersive spectroscope (EDS; 7421, Oxford Instruments, Bucks, U.K.). Dielectric properties in microwave range (5-7 GHz) were measured by parallel conducting plate method and SRF temperature coefficient (τ_f) of specimens were measured at 25-80 ºC by cavity method[3].

RESULTS AND DISCUSSION

Fig. 1 shows XRD patterns of BZNT with variation of calcination temperature. Crystal structure of BZNT is reported to have orthorhombic pyrochlore[4]. According to Hong *et al.*[5], it is reported that BZNT has monoclinic symmetry (as known as L-BZT) under 950 ºC and then monoclinic peak in XRD pattern is splitted above that temperature till 1,100 ºC and this crystalline phenomenon is known as H-BZT. In Fig. 1(a) which shows specimen calcined at 800 ºC, secondary phase of $BiNbO_4$ can be observed and the peak intensity of that phase decreased with increase of Ta amount. In Fig. 1(b) which shows specimen calcined at 900 ºC, all the peaks accorded with those reported by Hong *et al.*[5] and Levin *et al.*[6] According to their results, this peaks shows monoclinic zirconolite-like structure in C2/c space group. Secondary phase of $BiNbO_4$ did not appeared at 900 ºC and peaks in the range of 33-35º was splitted as reported by Hong *et al.*[5]. It is known that this phenomenon comes from lattice distortion by repulsion among isolated electron pairs[4] in Bi^{3+}. When specimens were sintered at 900 ºC with various amount of Ta (0.3-1.0 mol) using powders calcined at 900 ºC, any secondary phase was not observed and monoclinic structure was kept. It is thought that Ta ion substitution did not affect crystal structure significantly, for peaks were not shifted though Nb ions had been substituted by Ta ions. The reason is thought that ion radii of both Nb and Ta ion are similar as 0.64 Å.

Fig. 2 shows microstructures of sintered specimens with variation of Ta amount. Neither secondary phase nor liquid phase was observed and size of crystallite appeared to decrease with increase of Ta amount. Remarkable decrease was observed at x = 0.5. This is thought to be due to the change of main phase from BZN to BZT. While it is known that large crystallite generally shows superior dielectricity, it is thought that high quality factor of Ta makes BZNT show superior dielectricity even with small crystallite.

Fig. 3 shows density change of sintered bodies with variation of Ta amount. Specimens were sintered at various temperature for 2 h with powders calcined at 900 ºC. As Ta amount increased, density also increased, while sintering temperature did not make notable density difference.

Figs. 4 and 5 shows dielectric properties of specimens sintered at various temperatures with variation of Ta amount. As Ta amount increased, Qf_0 increased till x = 0.5 then decreased, while dielectric constants decreased from 77 to 63. With sintering temperature variation, dielectric constants did not change so much, but Qf_0 changed sensitively. With Ta amount of 0.0 and 0.3, Qf_0 increased with increase of sintering temperature from 850 to 900 ºC, but above that temperature Qf_0 decreased at 950 ºC and 1,000 ºC. With Ta amount above 0.3

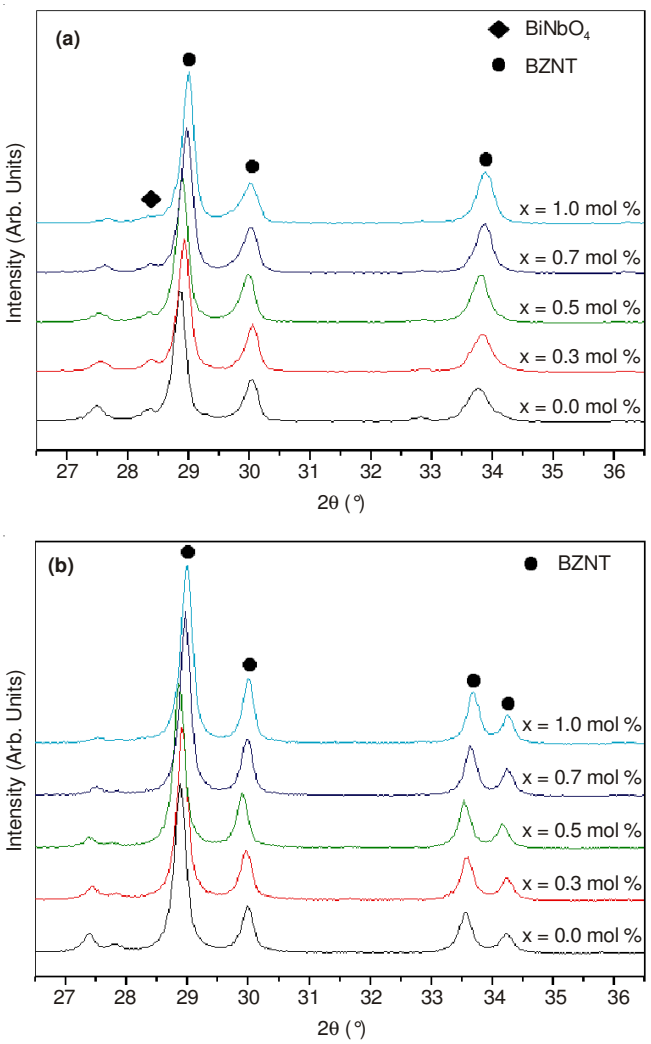

Fig. 1. XRD Patterns of $Bi_2[Zn_{1/3}(Nb_{1-x}Ta_x)_{2/3}]_2O_7$ calcined at (a) 800 ºC and (b) 900 ºC for 2 h

(*i.e.*, 0.5, 0.7, 1.0), Qf_0 increased with increase of sintering temperature. This phenomenon accords with the report that BZN shows superior dielectricity at 850 ºC, while BZT containing Ta, which has high melting temperature and preferable loss characteristic[4] at 1,050 ºC. From this result, it is thought that main composition changed from BZN to BZT at x = 0.5. According to previous report, $BiNbO_4$ appears at 750 ºC in BZN system[7] and Qf_0 was 2,9803, ε_r was 76 with sintering temperature[6] of 950 ºC. In BZT system, Qf_0 was 3,2003, ε_r was 66 with sintering temperature[5] of 850 ºC. In BZNT (x = 0.5) system of this study, Qf_0 was 4,2293, ε_r was 71 with sintering temperature of 900 ºC, which are superior dielectric properties.

Fig. 6 shows SRF temperature coefficients (τ_f) measured at 900 and 1,000 ºC with variation Ta substitution amount. As Ta amount increased, value of τ_f changed from negative to positive region near '0'. After BZN and BZT were calcined at 900 ºC and then sintered at 900 ºC respectively, microwave dielectric properties of BZN were Qf_0 = 3,584GHz, ε_r = 77 and τ_f = -34.2 ppm/ºC. Those of BZT were Qf_0 = 3,640 GHz, ε_r = 64 and τ_f = 2.2 ppm/ºC. From this, it is thought that as Ta amount increased, τ_f changed from negative to positive region. BZT has superior Qf_0 to BZN, but higher sintering temperature

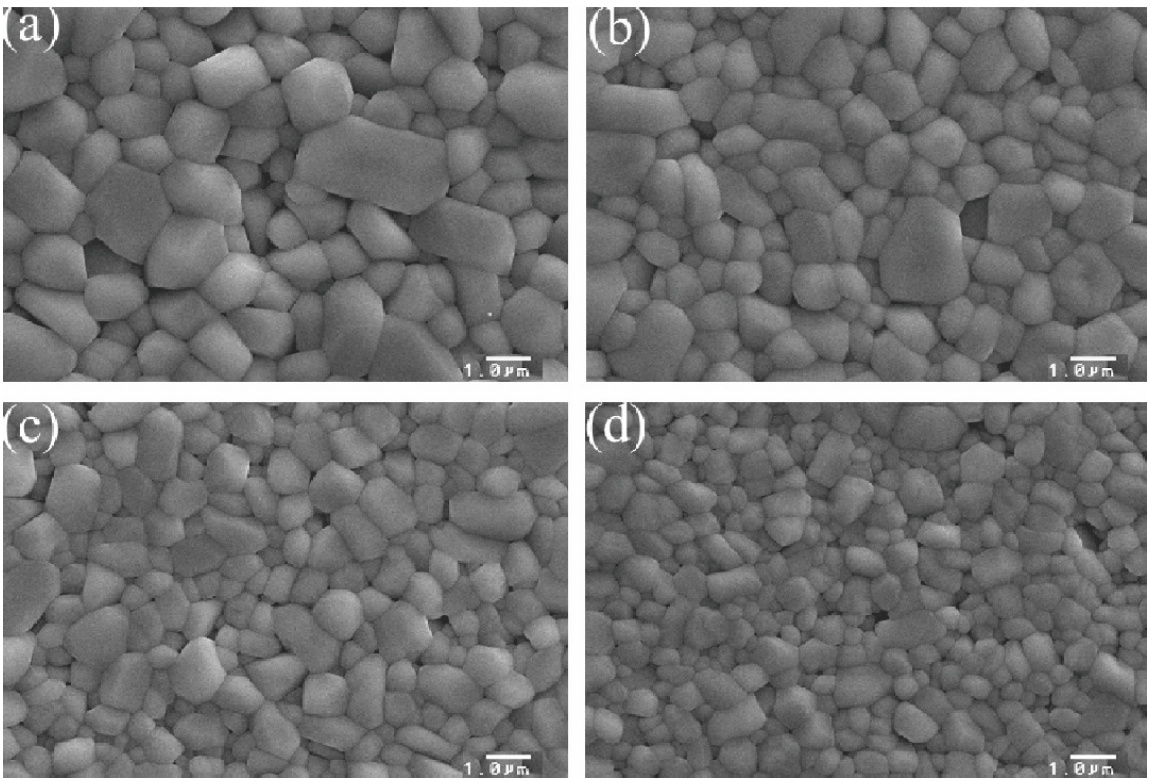

Fig. 2. SEM micrographs of the $Bi_2[Zn_{1/3}(Nb_{1-x}Ta_x)_{2/3}]_2O_7$ specimens with (a) x = 0, (b) x = 0.3, (c) x = 0.5 and (d) x = 1.0 sintered at 900 ℃ for 2 h

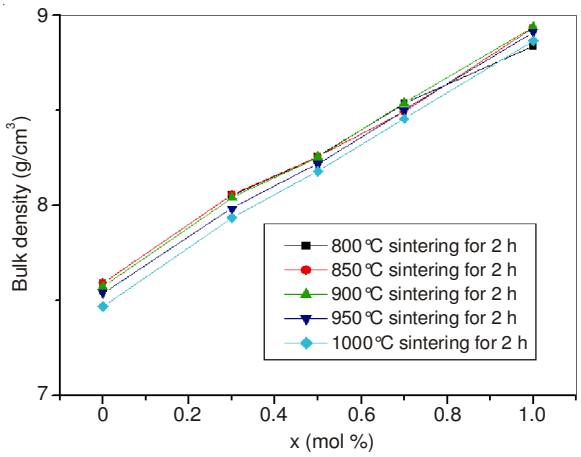

Fig. 3. Bulk density of $Bi_2[Zn_{1/3}(Nb_{1-x}Ta_x)_{2/3}]_2O_7$ samples as a function of sintering temperature

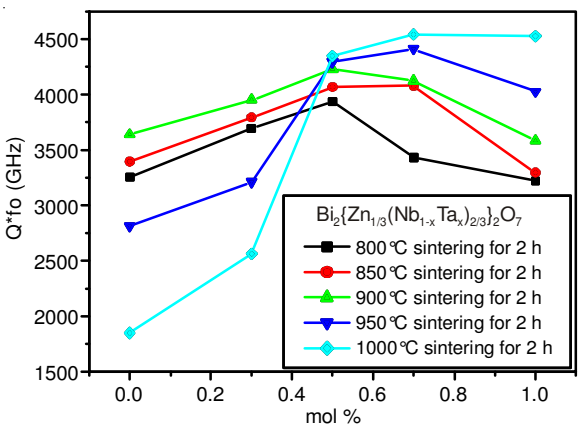

Fig. 4. Qf_0 of $Bi_2[Zn_{1/3}(Nb_{1-x}Ta_x)_{2/3}]_2O_7$ as a function of sintering temperature

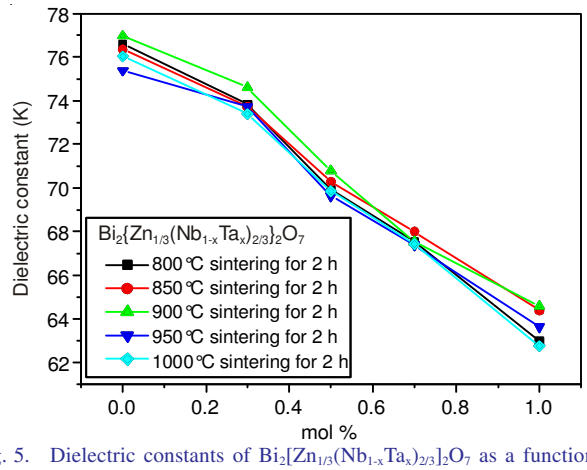

Fig. 5. Dielectric constants of $Bi_2[Zn_{1/3}(Nb_{1-x}Ta_x)_{2/3}]_2O_7$ as a function of sintering temperature

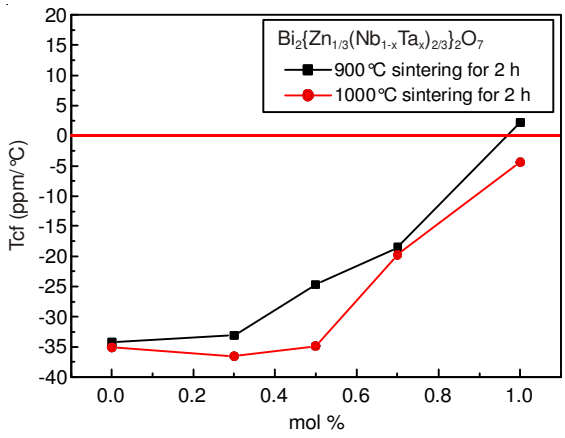

Fig. 6. Temperature coefficient of resonant frequency of $Bi_2[Zn_{1/3}(Nb_{1-x}Ta_x)_{2/3}]_2O_7$ as a function of Ta substitution contents

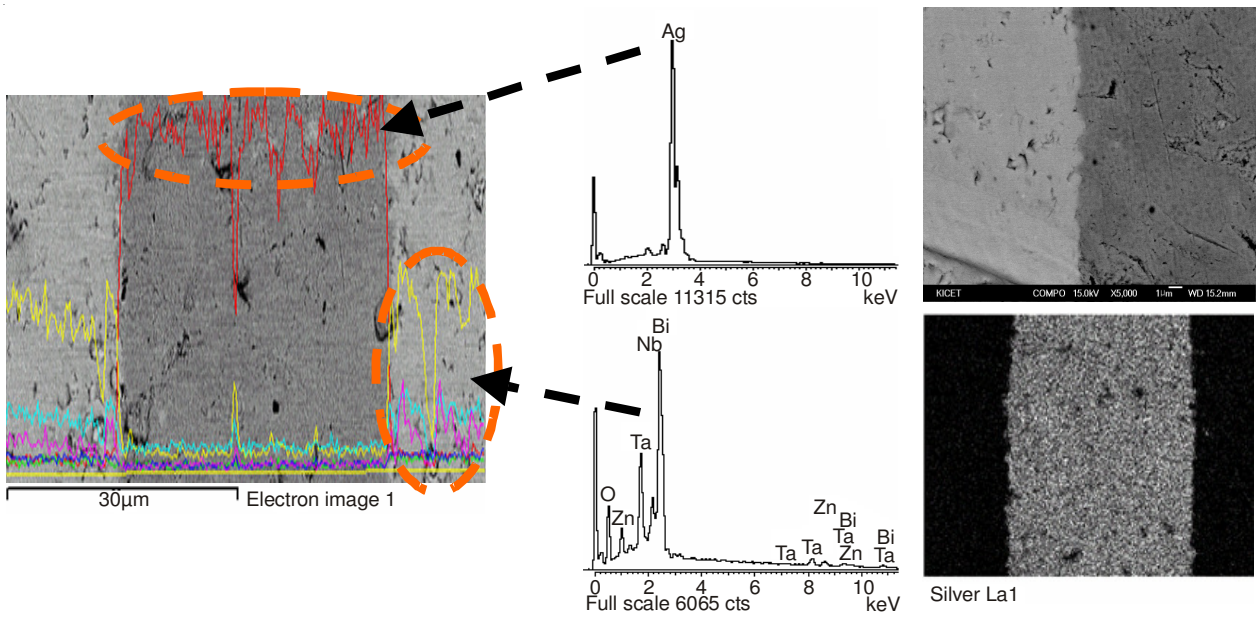

Fig. 7. SEM micrograph and EDS line scan of the interface between a silver electrode and $Bi_2[Zn_{1/3}(Nb_{1-x}Ta_x)_{2/3}]_2O_7$ (x = 0.5 mol %) co-fired at 900 ºC for 2 h

which make BZT difficult for co-firing with Ag electrode, while BZN can be co-fired with Ag electrode, but lower Qf_0 than BZT. Therefore in this study, BZNT, solid solution between BZT and BZN, was synthesized and sintered at 900 ºC and showed superior dielectric properties of Qf_0 = 4,229 GHz and ε_r = 71 with x = 0.5.

Fig. 7 shows EDS result at interface region of co-fired Ag electrode and BZNT (x = 0.5) which was sintered at 900 ºC. It can be known that there was neither diffusion nor reaction between two composition and BZNT (x = 0.5) was thought to be feasible for LTCC application.

Conclusion

After BZN and BZT were calcined at 900 ºC and then sintered at 900 ºC, respectively, microwave dielectric properties of BZN were Qf_0 = 3,584 GHz, ε_r = 77 and τ_f = -34.2 ppm/ºC. Those of BZT were Qf_0 = 3,640GHz, ε_r = 64 and τ_f = 2.2 ppm/ºC. BZNT ($Bi_2[Zn_{1/3}(Nb_{1-x}Ta_x)_{2/3}]_2O_7$), synthesized from BZN and BZT, has monoclinic symmetry and shows superior microwave dielectric properties of Qf_0 = 4,229 GHz, ε_r = 71 and τ_f = 24.7 ppm/ºC with x = 0.5. This composition showed neither diffusion nor reaction with Ag electrode after co-firing and is thought to be feasible for LTCC application.

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