Microwave Dielectric Properties of Sb$_2$O$_3$ Substituted BiNbO$_4$ Ceramics

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The microwave dielectric properties of BiNb$_{1-x}$Sb$_x$O$_4$ ceramics were investigated as a function of Sb$^{+5}$ substitution (0.01 $\leq x \leq 0.1$). BiNb$_{1-x}$Sb$_x$O$_4$ compositions containing sintering additives of 0.03 wt% CuO and 0.07 wt% V$_2$O$_5$ were prepared at low temperature (880°C to 960°C). Single orthorhombic (α-BiNbO$_4$) phase in all BiNb$_{1-x}$Sb$_x$O$_4$ compositions was obtained under all sintering temperature. The dielectric constant ($\varepsilon_r$) ranged from 41.8 to 44.7 according to Sb content. The Q-f$_s$ values of BiNb$_{1-x}$O$_4$ ceramics ranged from 14,000 to 42,000. As increasing the Sb content, the temperature coefficient of resonant frequency ($\tau_f$) was shifted to negative value between $-7$ ppm/°C and $-26$ ppm/°C.

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1. Introduction

Along with the rapid development of mobile communication system, the interest in the size reduction of microwave devices has been significantly increased. In order to reduce the size of the microwave devices, dielectric components must be also miniaturized. Multilayer component using low temperature cofired ceramics (LTCC) technology to meet with this purpose has been developed. Dielectric ceramics for the multilayer chip component is desirable using a low resistance conductors such as Ag (961°C) and Cu (1064°C). In general, the required characteristics for microwave dielectric materials are high dielectric constants ($\varepsilon_r$), high quality factor values (Q-f$_s$), and lower temperature coefficient of the resonant frequency ($\tau_f \leq 10$ ppm/°C). The sintering temperatures of conventional dielectric ceramics are ranging from 1200°C to 1500°C. However, this temperature region is much higher than the melting temperature of Ag and Cu used as an inner electrode. Therefore, the conventional dielectric ceramics compositions can not be co-fired together with Ag and Cu electrodes to reach proper densification.

In order to decrease the sintering temperature of the microwave dielectrics, the several approaches have been applied. Main efforts were (1) addition of a low firing additives, (2) changing the chemical prehistory to reduce a particle size of starting materials. Bismuth based oxide ceramics are one of attractive microwave dielectrics due to relatively low sintering temperature of 880°C. The bismuth based dielectrics have been also studied for the applications like as multilayer capacitors and piezoelectric devices.

The microwave property of the Bi$_2$O$_3$-Nb$_2$O$_5$ system was first reported by Kagata et al. After his study, BiNbO$_4$ based dielectrics substituted with Nd$_2$O$_3$ and Ta$_2$O$_5$ to Bi$_2$O$_3$ were studied by several groups. Bismuth based oxide ceramics are one of attractive microwave dielectrics due to relatively low sintering temperature of 880°C. The bismuth based dielectrics have been also studied for the applications like as multilayer capacitors and piezoelectric devices.

2. Experimental procedure

High purity (> 99.9%) of Bi$_2$O$_3$, Nb$_2$O$_5$, Sb$_2$O$_3$, CuO and V$_2$O$_5$ were used as starting materials. The BiNb$_{1-x}$Sb$_x$O$_4$ powders (0.01 $\leq x \leq 0.1$) were prepared by a conventional solid-solution reaction method. The powders were mixed with ZrO$_2$ ball for 24 h in ethanol and then dried After calcination of the dried powders at 800°C for 2 h in air. The calcined powder was milled together with the sintering additives of 0.03 wt% CuO and 0.07 wt% V$_2$O$_5$ and then dried again. The re-dried powder was sieved through 80 mesh screen, and pressed uniaxially into pellets of 12 mm in diameter and ~5 mm in thickness, and then cold isostatically pressed at 20,000 psi. The samples were sintered from 880°C to 960°C for 2 h, respectively.

X-ray diffraction (CuKα radiation, D/Max 2500, Rigaku) was carried out on the powders obtained by crushing the sintered specimens for phase identification. Microstructure of the samples was observed using a scanning electron microscope (SEM, S-4200, Hitachi). Bulk density was also measured by the Archimede’s method. The microwave dielectric properties were measured by Hakki and Coleman method using Network Analyzer (HP8720C). As not all specimens were available in equal size, the properties were measured at different frequencies. The temperature coefficient of resonant frequency ($\tau_f$) at microwave frequencies was measured in the temperature range of 20°C to 80°C.

3. Results and discussion

The X-ray diffraction patterns of BiNb$_{0.97}$Sb$_{0.03}$O$_4$ ceramics calcined at 800°C for 2 h and sintered from 880°C to 960°C for 2 h are shown in Fig. 1. BiNbO$_4$ has the crystal structure of orthorhombic stibontantale type (low temperature α-BiNbO$_4$...
form) below 1020°C and then transforms to the triclinic phase (high temperature β-BiNbO₄ form) above 1020°C. This transformation is irreversible. The peaks of calcined powder at 800°C were indexed based on the α-BiNbO₄ orthorhombic phase as a main phase, Bi₂Nb₂O₇ and Bi₂NbO₆O₁₇ were also appeared as the second phase. After sintered from 880°C to 960°C for 2 h, single phase of the α-BiNbO₄ orthorhombic type was revealed. The crystalline phases of the BiNb₁₋ₓSbₓO₄ system sintered at 920°C for 2 h were investigated as shown in Fig. 2. Even though the amount of Sb content is increased, transformation to triclinic phase is not detected. The second phase is not observed either. All compositions showed only a single phase based on α-BiNbO₄ type orthorhombic phase.

Figure 3 shows the variation of apparent bulk density as a function of sintering temperatures according to Sb substitution content. Without additive, only below 81% theoretical density was obtained at 960°C for 2 h. However, by adding of 0.03 wt% CuO and 0.07 wt% V₂O₅ to BiNb₁₋ₓSbₓO₄ ceramics, 95% relative density was reached at all sintering temperatures. The bulk densities of BiNb₁₋ₓSbₓO₄ ceramics were increased largely with increasing of sintering temperatures until 920°C. But, the bulk densities were slightly increased at 940°C and then slightly decreased at 960°C. The microstructure of the BiNb₀.₈₇Sb₀.₀₃O₄ ceramics as a function of the sintering temperatures is shown in Fig. 4. At all sintering temperature range, BiNb₀.₈₇Sb₀.₀₃O₄ ceramics were dense (> 95% theoretical density). As increasing the sintering temperatures, grains were grown. However, when sintering temperature is over 920 °C, abnormal grain growth and pores were distinctly observed. So, the optimum firing condition for the BiNb₀.₈₇Sb₀.₀₃O₄ sample was 920°C.

The dielectric constant (εᵣ) data of the BiNb₁₋ₓSbₓO₄ ceramics were plotted in Fig. 5. The εᵣ value of BiNb₁₋ₓSbₓO₄ cer-
amics increased rapidly at lower sintering temperature range. But the $\varepsilon_r$ values of BiNb$_{1-x}$Sb$_x$O$_4$ ceramics increased slightly at higher sintering temperatures. The larger increase of the $\varepsilon_r$ value of BiNb$_{1-x}$Sb$_x$O$_4$ ceramics at lower sintering temperature range is resulted from the main effect of grain growth and reduction of porosity. Slight increase of the $\varepsilon_r$ values of BiNb$_{1-x}$Sb$_x$O$_4$ ceramics at higher sintering temperatures would be due to the relation of the abnormal grain growth and formation of small sized pores as typically shown in Fig. 4(d) and 4(e). On the whole, the dielectric constants showed similar tendency to apparent density variation. As increasing of Sb substitution content, the $\varepsilon_r$ values of BiNb$_{1-x}$Sb$_x$O$_4$ ceramics increased and saturated between 43.0 and 44.7 at 960°C.

Figure 6 shows the Q-f$_0$ values of the BiNb$_{1-x}$Sb$_x$O$_4$ compositions as a function of the sintering temperature. The Q-f$_0$ values were increased as increasing the sintering temperature and reached maximum at 920°C, and then decreased as increasing the sintering temperature. The largest Q-f$_0$ values was 41,800 at $x=0.025$. There are many factors to affect the resultant dielectric loss in the microwave dielectric materials. The intrinsic loss of dielectric loss is caused by anharmonic phonon decay processes in pure crystal. The extrinsic loss of dielectric loss is caused by point defects, dopant elements and vacancy in real crystal, while the extrinsic loss is also caused by dislocations, grain boundary, pores and second phases in the sintered ceramics. The reason of Q-f$_0$ values decreased here was due to the increased abnormal grain growth as mentioned in the microstructure. The Q-f$_0$ values were increased below 920°C except $x=0.1$, since the grain size was increased and the grain boundary was reduced, while the Q-f$_0$ values decreased due to grow the abnormal grain growth. Considering the relationship between the amount of Sb content and the Q-f$_0$ values, the Q-f$_0$ value reached at maximum value when the Sb content was 0.025 and then critically decreased as the Sb content increased. This result is assumed that the relationship with the XRD results (Fig. 2). Intensity of the XRD peaks of (040) and (080) were increased and reach a maximum at 0.025 mol% Sb content. After that intensity of XRD peaks of (040) and (080) were decreased with the increase of Sb content as shown in Fig. 2. According to Kawashima et al.\textsuperscript{15}, the Q-f$_0$ value is increased by lattice ordering. It could not be surely explained that this seems to be the result of b-axis lattice ordering. Because there are a lot of factors affected to the dielectric loss in microwave dielectric materials. It would be assumed that the intensity of the XRD peaks of (040) and (080) would be increase, if the rate of b-axis lattice ordering increased.

The composition dependence of resonant frequency ($\tau_f$) in the BiNb$_{1-x}$Sb$_x$O$_4$ System sintered at 920°C illustrated in Fig. 7. As the Sb content is increased, the $\tau_f$ is negatively increased. The $\tau_f$ values are varied from $-7$ ppm/°C to $-26$ ppm/°C.

4. Conclusion

In this study, the microwave dielectric properties of BiNb$_{1-x}$Sb$_x$O$_4$ ceramics with the sintering additives of 0.03 wt% CuO and 0.07 wt% V$_2$O$_5$ were investigated as a function of amount of Sb$^{3+}$ substitution ($0.01 \leq x \leq 0.1$). As increasing the Sb$^{3+}$ content, the dielectric constants and bulk density were increased. The quality factor showed the maximum value in the BiNb$_{0.97}$Sb$_{0.03}$O$_4$ ceramics fired at 920°C, and the temperature coefficient of the resonant frequency shifts to negative value as increasing the Sb$^{3+}$ content. The dielectric constant ($\varepsilon_r$) of all compositions ranged from 41.8 to 44.7. Q-f$_0$ values of BiNb$_{1-x}$Sb$_x$O$_4$ ceramics were greatly improved compared to the BiNbO$_2$ ceramics. The $\varepsilon_r$ values of 41.8 to 44.7 and the Q-f$_0$ values of 14,000 to 42,000 and $\tau_f$ of $-7$ ppm/°C to $-26$ ppm/°C were obtained.

References

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