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Microwave dielectric properties of $BiNbO_4$ ceramics with $CuO–V_2O_5$ addition

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Abstract

$BiNbO_4$ ceramics were developed by using $CuO–V_2O_5$ as a liquid phase sintering agent. The resultant dielectric properties were analyzed in terms of the densification and the amount of $CuO–V_2O_5$ sintering agent. The addition of 0.8 wt.% $CuO–V_2O_5$ as its sintering agent was observed to perform most satisfactory. At 850 °C, uniform and enhanced microstructure was observed for the $BiNbO_4$ specimen with 0.8 wt.% $CuO–V_2O_5$ addition. Furthermore, the effect of $CuO–V_2O_5$ addition on the microwave dielectric properties of $BiNbO_4$ was also investigated. As the sintering temperature increased to 900 °C, the dielectric constant increased but nearly constant and the quality factor (*QF*) showed a maximum at 850 °C and then decreased for all compositions of the 900 °C sintered specimens. With an increase in $CuO–V_2O_5$ content, the temperature coefficient of frequency (*TCF*) increased in accordance with the dielectric mixing rule and microstructural behavior.

Keywords: A. Sintering; C. Dielectric properties; Chemical synthesis; Microstructure

1. Introduction

With the rapid progress in commercial wireless communication, the miniaturization of mobile communication terminals and components has become increasingly important. The application of multilayer microwave devices will contribute to the realization of this aim [1]. So far effort has been concentrated on the fabrication of a dielectric material within the multilayered integrated circuit. During the fabrication of multilayer microwave devices, low-firing microwave dielectric materials with high *QF* values are necessary for its co-firing process with low-loss, low-melting point conductors such as silver and copper. The most popular method of achieving this goal involves, both using low temperature sintering agents and mixing compositions with different dielectric properties [2,3]. By combining two or more components, a near-zero *TCF* and high *QF* values can be obtained.

Numerous dielectric compounds including Nb_2O_5 and their solid solutions have been investigated in the microwave frequency range [4–6]. The niobate based materials are candidates for microwave dielectrics due to their low cost and high quality factor [6]. Among a large number of niobate based compositions, $BiNbO_4$ was selected for this study. $BiNbO_4$ exhibits a dielectric constant of ~40, a *QF* ~10,000 GHz, and a *TCF* ~+15 ppm/°C [7]. $BiNbO_4$ ceramics can be sintered at low temperature and still have good microwave dielectric properties. Their sintering temperature can be controlled by a small addition of $CuO–V_2O_5$ as a sintering agent [8]. However, a systematic investigation of compositional details, the dielectric properties of $BiNbO_4$ ceramics and sintering agents are necessary for designing dielectric compositions. Moreover, a modification of the *TCF* is necessary because of the large negative value of the coefficient. Because of the high *QF* and negative *TCF* value of $BiNbO_4$, an appropriate mixture of $BiNbO_4$ and $CuO–V_2O_5$ could be expected to provide both a high *QF* value and temperature stable resonant frequency. In this study, the influence of CuO–

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V_2O_5 as a sintering agent on the microwave dielectric properties of $BiNbO_4$ was investigated as a function of sintering temperature and composition.

2. Experimental procedures

Mixed oxide powders of $BiNbO_4$ with $CuO–V_2O_5$ as a sintering agent were prepared from Bi_2O_3, Nb_2O_5, CuO and V_2O_5 with purity higher than 99.5% by a conventional mixed-oxide method. First, $BiNbO_4$ was synthesized through the calcination of $Bi_2O_3–Nb_2O_5$ at 750 °C for 3 h. CuO and V_2O_5 were also calcined in order to synthesize $CuO–V_2O_5$ as the sintering agent at 500 °C for 5 h. The final compositions were batched and then wet mixed with ZrO_2 balls for 24 h in ethanol. After drying, the reagent was calcined at 800 °C for 3 h. The calcined powders were milled again with ZrO_2 balls for 24 h in ethanol and then sieved using an 80-mesh screen. Prepared powders were dried in an oven (100 °C) for 24 h and pressed into disks, where a pressing pressure of 1450 kg/cm^2 was used for all specimens in the cold isostatic pressing process. Specimens were then sintered at 830–920 °C for 3 h at a heating rate of 200 °C/min. Crystalline phases of the sintered specimens were identified by X-ray powder diffraction (Rigaku D/Max-3 C, Japan) using Cu Kα radiation (λ = 1.5418 Å) with 40 kV/30 mA, a sampling width of 0.02°, and scan speed of 4°/min in the 2θ range of 10–80°. Microstructures of the specimens were studied by scanning electron microscopy (SEM, Hitachi S-4200, Japan). Microwave dielectric properties of the specimens were measured by the post resonant method using the TE_{011} mode [9].

3. Results and discussion

Fig. 1 shows the DTA curve of $BiNbO_4$ powders for a heating rate of 5 °C/min.

Fig. 2 shows the XRD patterns of $BiNbO_4$ calcined at 850 °C and 1150 °C for 3 h, showing orthorhombic and triclinic crystal structures, respectively. In these figures, the phase change from the low temperature orthorhombic phase to the high temperature triclinic phase can be observed as its temperature increases and the phase transition temperature seems to be about 1079 °C. In this work, therefore, the effect of $CuO–V_2O_5$ on the sintering behavior was studied for the composition of $BiNbO_4$ in order to lower the sintering temperature to ~850 °C,

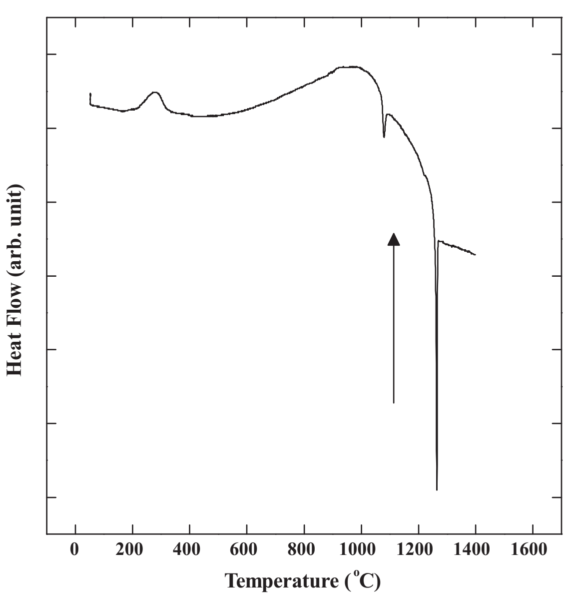

Fig. 1. DTA curves of $BiNbO_4$ powders. (heating rate: 5 °C/min).

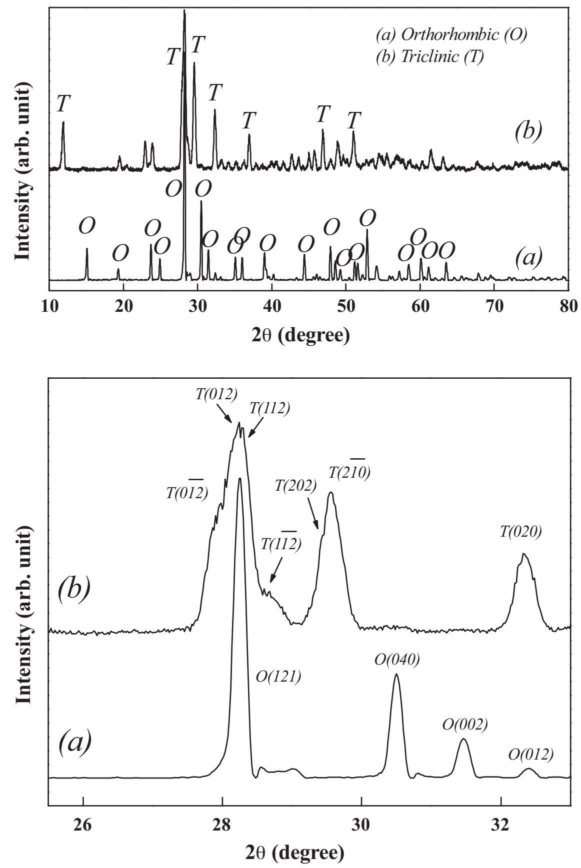

Fig. 2. XRD patterns of $BiNbO_4$ specimens calcined (a) at 850 °C for 3 h and (b) at 1150 °C for 3 h, showing crystal structures of orthorhombic and triclinic, respectively.

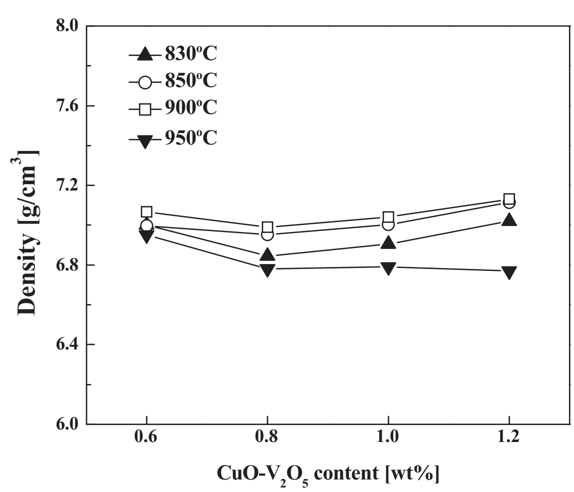

Fig. 3. Bulk density of $BiNbO_4$ specimens as a function of $CuO–V_2O_5$ content sintered at 830–900 °C for 3 h.

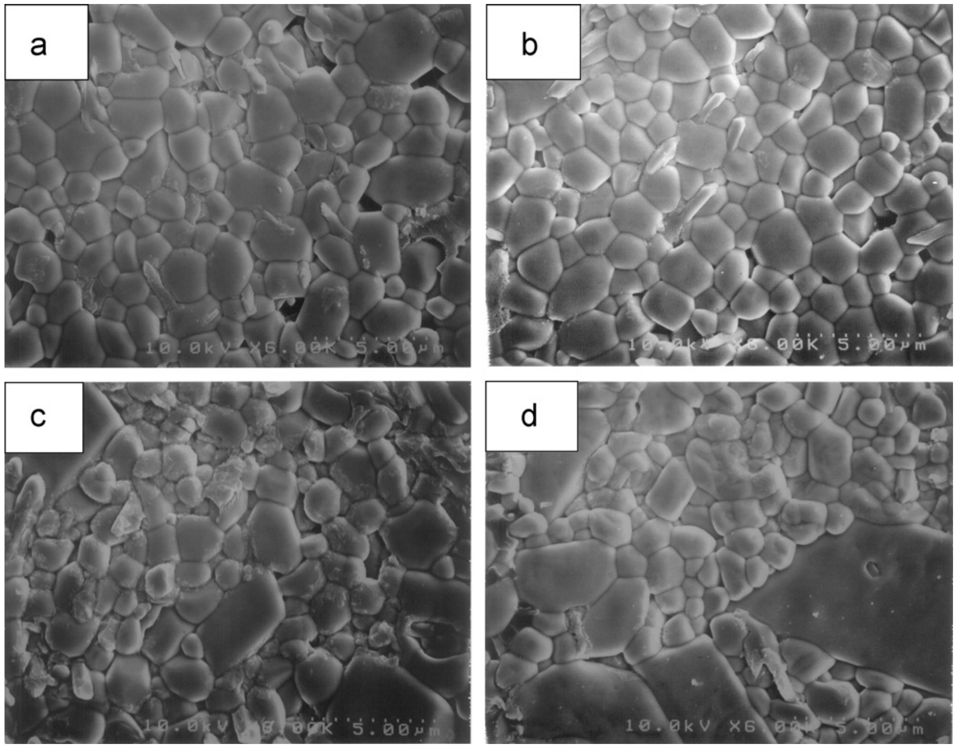

Fig. 4. SEM micrographs of $BiNbO_4$ specimens as a function of $CuO–V_2O_5$ content; (a) 0.6 wt.%, (b) 0.8 wt.%, (c) 1.0 wt.%, (d) 1.2 wt.% sintered at 850 °C for 3 h.

for a possible co-firing process with internal conductors below the melting temperature of the metals such as Ag and Cu. The bulk densities of the $BiNbO_4$ specimens as a function of $CuO–V_2O_5$ content and sintering temperature are given in Fig. 3. Except for the 950 °C sintered specimens, the densities of the specimens remain initially almost unchanged and then increase a little with increasing $CuO–V_2O_5$ content due to the low melting point of $CuO–V_2O_5$ (m.p. = 650 °C) [10]. Fig. 3 also shows the densities as a function of sintering temperature. With an increase of sintering temperature, the low temperature

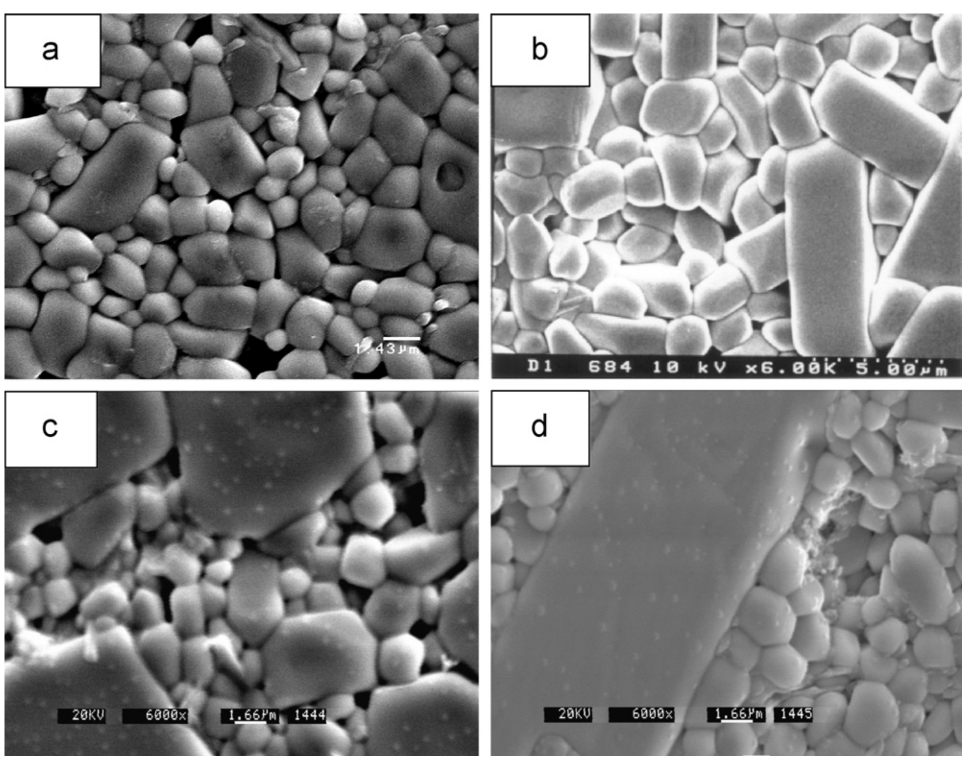

Fig. 5. SEM micrographs of $BiNbO_4$ specimens as a function of $CuO–V_2O_5$ content; (a) 0.6 wt.%, (b) 0.8 wt.%, (c) 1.0 wt.% and (d) 1.2 wt.% sintered at 900 °C for 3 h.

sintering behavior appears effectively with the addition of CuO–V_2O_5 and reaches a maximum value at 900 °C. This figure shows that the densification with CuO–V_2O_5 at 900 °C is higher than that at 950 °C, which suggests that a temperature higher than 900 °C is unnecessary. This result reveals that a significant reduction in the sintering temperature of $BiNbO_4$ is possible with CuO–V_2O_5 addition as a sintering agent while maintaining high density.

Figs. 4 and 5 show the SEM micrographs of $BiNbO_4$ ceramics with different amounts of CuO–V_2O_5 addition, and sintered for 3 h at 850 °C and 900 °C, respectively. When sintered at 850 °C, a small and regular grain size (1–3 μm) was easily observed for the 0.6 and 0.8 wt.% CuO–V_2O_5-added specimens. However, in Fig. 4(c) and (d), abnormal grain growth could be detected, and this behavior seems to be the result of the liquid phase sintering due to the melting of CuO–V_2O_5. In Fig. 5, the abnormal grain growth due to liquid phase sintering is observed even in the specimen of 0.8 wt.% CuO–V_2O_5. Moreover it occurs more strongly than in Fig. 4 because of the higher sintering temperature. It seems that Cu and V form liquid phases during the sintering stage. For liquid phase sintering, the liquid phase is resident or disappears in the final stages. This suggests that the secondary phase could appear at the grain boundary or inside the grain, and that the phases would be rich in Cu and V. However, the secondary phases were not identified by XRD since detection of a minor phase by XRD was extremely difficult and its composition was very complex [11], and, therefore, further research is required. This fact is in accord with a previous report which suggested the formation of a residual phase containing Cu as the liquid phase of CuO-doped $BiNbO_4$ ceramics [12].

Fig. 6 shows the microwave dielectric properties of $BiNbO_4$ ceramics with CuO–V_2O_5 addition sintered at 850 °C and 900 °C for 3 h. The dielectric constants are nearly constant, and the *QF* values decrease with an increasing addition of CuO–V_2O_5. After reaching a maximum at the composition of 0.8 wt.% CuO–V_2O_5, the *QF* decreases when sintered at 850 °C. The *QF* values are generally known to be affected by the morphology of the specimens such as grain size and uniformity. Therefore, the decrease in its *QF* is thought to be due to the non-uniform microstructure caused by the abnormal grain growth resulting from liquid phase densification seen in Figs. 4 and 5. The *TCF* increased gradually with increasing CuO–V_2O_5 content. The *TCF* is known to be related to the composition and the second phase of the ceramic samples. No significant difference was observed in the *TCF* value between the specimens prepared at different sintering temperatures. However, the *TCF* value become more positive with increasing CuO–V_2O_5 content due to the effect of V_2O_5 and the subsequent formation of its liquid phase in sintering stage. This is in agreement with the reports of the previous studies on $BiNbO_4$ and $MgNb_2O_6$ ceramics [13,14]. Therefore, it is believed from this result that the *TCF* value of $BiNbO_4$ ceramics can be adjusted to near-zero by carefully controlling the content of CuO–V_2O_5.

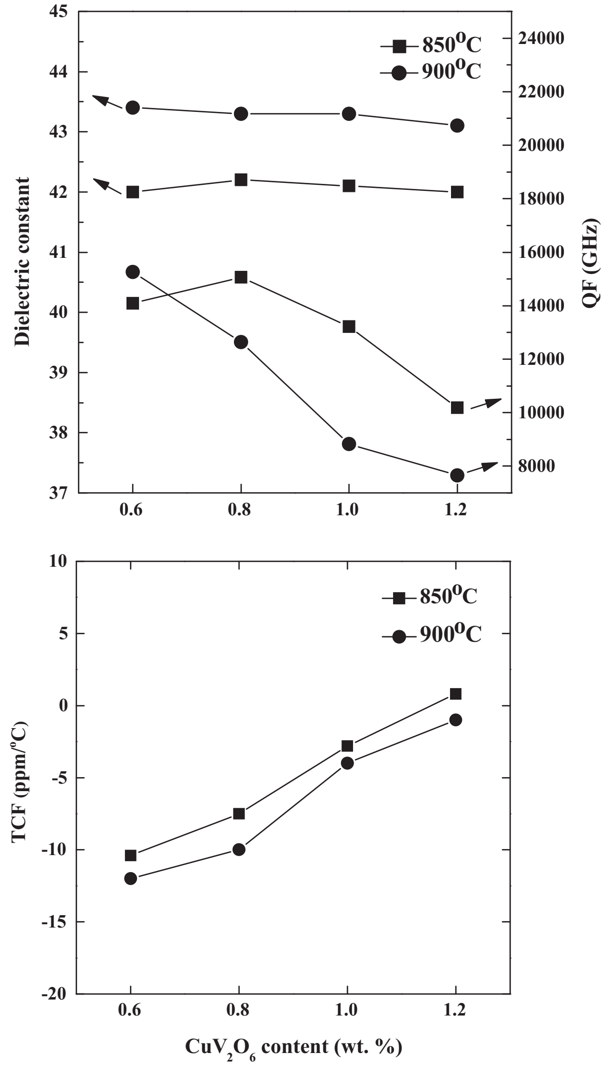

Fig. 6. Dielectric constant, quality factor (QF) and temperature coefficient of resonant frequency (TCF) of $BiNbO_4$ specimens sintered at 850 and 900 °C for 3 h as a function of CuO–V_2O_5 content.

4. Conclusion

The addition of CuO–V_2O_5 as a sintering agent to $BiNbO_4$ lowered the sintering temperature to 850–900 °C. The dielectric constants remain almost constant and the *QF* values of the specimens with CuO–V_2O_5 changed with increasing CuO–V_2O_5 content. This can be attributed to the occurrence of liquid phase densification. The *TCF* increased gradually with increasing CuO–V_2O_5 content. Therefore, it is suggested that the *TCF* of $BiNbO_4$-based ceramics can be adjusted to near-zero by carefully controlling the content of CuO–V_2O_5. Typically, $BiNbO_4$ with 0.8 wt.% CuO–V_2O_5 sintered at 850 °C, showed the microwave dielectric properties of $\varepsilon = 42$, $QF = 15{,}500$ GHz and $TCF = -4$ ppm/°C.

References

[1] T. Ishizaki, M. Fujita, T. Uwano, H. Kagata, T. Uwano, H. Miyake, A very small dielectric planar filter for portable telephones, IEEE Transaction on Microwave Theory and Techniques 42 (11) (1994) 2017–2022.

[2] I. Burn, Low-firing dielectric composition, United States Patent #4845062, 1989.

[3] J.W. Choi, C.Y. Kang, S.H. Shim, S.J. Yoon, H.J. Kim, K.H. Yoon, Dielectric and patch antenna characteristics of new high-Q (1-x)($Al_{1/2}Ta_{1/2}$)O_2-x($Mg_{1/3}Ta_{2/3}$)O_2 ($0 \leq x \leq 1.0$), Materials Chemistry and Physics 79 (2003) 247–251.

[4] I.M. Reaney, E.L. Colla, N. Setter, Dielectric and structural characteristics of Ba- and Sr-based complex perovskites as a function of tolerance factor, Japanese Journal of Applied Physics Part 1 33 (1994) 3984–3990.

[5] E.L. Colla, I.M. Reaney, N. Setter, Effect of structural changes in complex perovskites on the temperature coefficient of relative permittivity, Journal of Applied Physics 74 (1993) 3414–3425.

[6] H. Hughes, D.M. Iddles, I.M. Reaney, Niobate based dielectrics suitable for third generation mobile phone base stations, Applied Physics Letters 79 (2001) 2952–2954.

[7] H.R. Lee, K.H. Yoon, E.S. Kim, Y.S. Cho, S.O. Yoon, T.H. Kim, Microwave dielectric properties of $BiNbO_4$–$NiNb_2O_3$ ceramics with CuO–V_2O_5 sintering agent, Journal of the Ceramic Society of Japan 112 (5) (2004) S1579–S1582.

[8] H. Kagata, T. Inoue, J. Kato, I. Kameyama, Low-fire bismuth-based dielectric ceramics for microwave use, Japanese Journal of Applied Physics 31 (1992) 3152–3155.

[9] B.W. Hakki, P.D. Coleman, A dielectric resonator method of measuring inductive capacities in the millimeter range, IEEE Transaction on Microwave Theory and Techniques 8 (1960) 402–410.

[10] P. Fleury, Sur le CuO–V_2O_5 system, Comptes Rendus de I'Académie des Sciences, Paris, Series C 263 (1966) 1375–1377.

[11] C.-L. Huang, R.-J. Lin, J.-J. Wang, Effect of B_2O_3 additives on sintering and microwave dielectric behaviors of CuO-doped $ZnNb_2O_6$ ceramics, Japanese Journal of Applied Physics 41 (2002) 758–762.

[12] C.-L. Huang, M.-H. Weng, C.-C. Yu, Low firable $BiNbO_4$ based microwave dielectric ceramics, Ceramics International 27 (2001) 343–350.

[13] W.-C. Tzou, C.-F. Yang, Y.-C. Chen, P.-S. Cheng, Improvements in the sintering and microwave properties of $BiNbO_4$ microwave ceramics by V_2O_5 addition, Journal of the European Ceramic Society 20 (2000) 991–996.

[14] C.-S. Hsu, C.-L. Huang, J.-F. Tseng, C.-Y. Huang, Improved high-Q microwave dielectric resonator using CuO-doped $MgNb_2O_6$ ceramics, Materials Research Bulletin 38 (2003) 1091–1099.