

LOW-FIRED BiNbO_4 MICROWAVE DIELECTRIC CERAMICS MODIFIED BY CuV_2O_6 ADDITION SINTERED IN N_2 ATMOSPHERE

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The sintering behavior, microstructure and microwave dielectric properties of BiNbO_4 ceramics sintered in N_2 with CuO and V_2O_5 additions were investigated. The CuO and V_2O_5 additives, acting as the sintering aids, could effectively lower the sintering temperature of BiNbO_4 ceramics. CuV_2O_6 , formed by the reaction between CuO and V_2O_5 with the mole ratio of 1:1 at 500°C , was more effective to realize low-temperature sintering of BiNbO_4 ceramics than the $\text{CuO-V}_2\text{O}_5$ mixture. It was found that the addition of 0.1 wt% CuV_2O_6 to BiNbO_4 lowered the sintering temperature to approx 880°C while maintaining 98.4 % theoretical density. Pure orthorhombic BiNbO_4 phase was obtained successfully in the cases of $\text{CuO-V}_2\text{O}_5$ mixture or CuV_2O_6 additions. The $\text{CuO-V}_2\text{O}_5$ mixture addition would cause inhomogeneous and abnormal grain growth resulting in the degradation of densities and dielectric properties of BiNbO_4 ceramics. By contrast, a uniform and dense microstructure was obtained in BiNbO_4 ceramics with CuV_2O_6 -addition, contributed to higher dielectric constant and quality factor. The BiNbO_4 ceramics with 0.5 wt% CuV_2O_6 addition sintered at 860°C for 2 h have good microwave dielectric properties (at 4.3 GHz): relative dielectric constant (ϵ_r) = 47, quality factor ($Q \times f$) = 11950 GHz.

INTRODUCTION

Increasing attention has been paid to the development of multilayer devices for microwave applications, since multilayer devices have promising the applications in reducing size and weight of mobile communication components. To meet the requirements of such small-sized devices, experiments have been carried out to co-fire dielectric materials sintered at low temperatures with the highly conductive metal electrodes, such as silver or copper, which has a low melting point of 961°C and 1064°C , respectively. However, most of the well-known commercial microwave dielectric materials, such as BaTi_4O_9 , $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ and $\text{MgTiO}_3\text{-CaTiO}_3$ (MCT), which exhibit high quality factors (Q) and low temperature coefficients of resonant frequency (τ_f), are not compatible with the silver or copper electrodes due to their high sintering temperatures ($>1300^\circ\text{C}$) [1-3]. A common method to reduce the sintering temperature of these dielectric materials is adopting the low-melting glasses [4-6]. In another approach, some researches focused on searching for the matrix systems with inherently low sintering temperature.

Bismuth-based dielectric ceramics are well known as the low-fired materials [7, 8]. The microwave dielectric properties of BiNbO_4 ceramics were first reported by Kagata and his co-workers [9]. However, two problems

have impeded its application in microwave multilayer devices. One problem was that BiNbO_4 reacts easily with silver electrodes. The other was that it is difficult to achieve dense ceramics in BiNbO_4 below 1100°C without sintering aids. For the purpose of applying BiNbO_4 ceramics in microwave multilayer devices, BiNbO_4 ceramics should be sintered in the low oxygen N_2 atmosphere in order to be co-fired with Cu electrode. Moreover, some oxides and their mixtures were added to BiNbO_4 , such as ZnO , B_2O_3 , CuO and V_2O_5 [9-13]. It turns out that the sintering temperature can be effectively reduced by ZnO or B_2O_3 additions, but the microwave dielectric properties of BiNbO_4 are deteriorated in this way. By contrast, BiNbO_4 ceramics can be densified at 875°C and have a higher Q value of 4260 (at 4.3 GHz) with the addition of CuO and V_2O_5 [14]. Therefore, the effects of CuO and V_2O_5 additions on the microstructure and microwave dielectric properties of BiNbO_4 ceramics have been a research focus. However, the reported research is limited to the doping effect of mechanical mixture of CuO and V_2O_5 and the sintering behavior of BiNbO_4 in air.

In this study, two kinds of $\text{CuO-V}_2\text{O}_5$ dopants were applied to reducing the sintering temperature of BiNbO_4 ceramics to compare their effects. One is the mechanical mixture of CuO and V_2O_5 , and the other is the compound of CuO and V_2O_5 . Besides, the sintering behavior in

N_2 and the microwave dielectric properties of CuO- V_2O_5 -doped $BiNbO_4$ ceramics were investigated. X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses were also applied to study the crystal structure and the microstructure of CuO- V_2O_5 -doped $BiNbO_4$ ceramics.

EXPERIMENTAL

Specimen powders were prepared by the conventional solid-state process. The starting materials were the high-purity Bi_2O_3 and Nb_2O_5 powders (>99.99 %). These powders were weighed according to the stoichiometry of 1:1 and ball-milled for 24 h with deionized water in the polyethylene jars. Then the mixtures were dried and calcined at 800°C for 3 h, the product being characterized as $BiNbO_4$ phase by XRD analysis. The $BiNbO_4$ powders was added with two kinds of CuO- V_2O_5 (CuO: V_2O_5 = 1:1 in mole ratio) complexes, respectively. One is the mechanical mixture (noted as CV-1) of CuO and V_2O_5 , ball-milled for 12 h, and the other is the compound (noted as CV-2) of CuO- V_2O_5 , which was ball-milled for 12 h and calcined at 500°C for 5 h. Powders of $BiNbO_4$ mixed with either CV-1 or CV-2 were re-milled for 24 h, and then pelleted to disks 18 mm in diameter and 9 mm in thickness with 6 wt.% PVA binder. Disks were sintered at 840 ~ 940°C for 2 h in N_2 .

Bulk density of the sintered ceramics was measured by using the Archimedes' method. Phases identification was carried out by using an X-ray diffractometer (Philips X'Pert Pro MPD) with Cu $K\alpha$ radiation over the range of $2\theta = 15 - 70^\circ$. Microstructures of the as-fired ceramics were observed by using a scanning electron microscopy (SEM, S-530 Hitachi). The dielectric constant ϵ_r and the quality factor Q at microwave frequencies were measured with a network analyzer (Model Agilent E8363A) by using Hakki-Coleman dielectric resonator method [12].

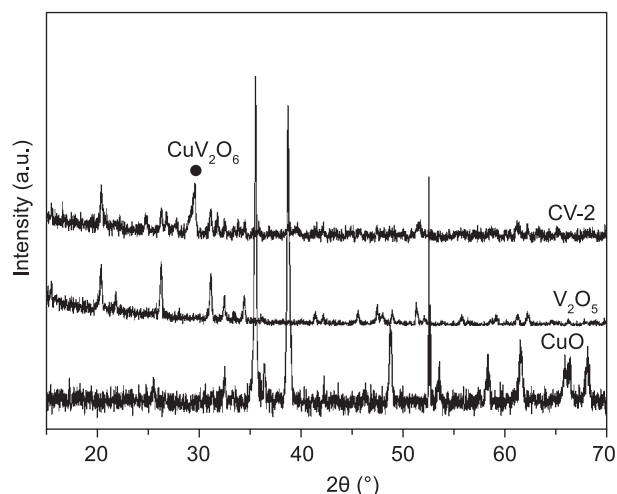


Figure 1. XRD patterns of CuO, V_2O_5 and CV-2 powders.

RESULTS AND DISCUSSION

The XRD patterns of CuO, V_2O_5 and CV-2 powders are shown in Figure 1. It is clearly observed that the diffraction peaks of CV-2 differ from those of either CuO or V_2O_5 . The main crystal phase of CV-2 powders is characterized as CuV_2O_6 , formed by the solid-state reaction between CuO and V_2O_5 . According to the phase diagram of CuO and V_2O_5 system [15], the melting point of CuO and V_2O_5 is 1300 °C and 670 °C, respectively. When CuO: V_2O_5 = 1:1 in mole ratio, a new compound CuV_2O_6 is formed, which has a lower melting point of 630°C. Therefore, compared with individual CuO or V_2O_5 , CuV_2O_6 is more effective to realize the low-temperature sintering.

The effects of CV-1 and CV-2 additions on the sintering behavior of $BiNbO_4$ ceramics in N_2 were investigated. Figure 2 shows the bulk density as functions of the sintering temperature and the content of dopant (CV-1 or CV-2). It is obvious that the sintering temperature is markedly reduced with the addition of CV-1 or CV-2. The bulk density increased, saturated, and then slightly decreased as the sintering temperature increased. The overall tendency showed that the density of the samples with CV-2 addition was higher than that with CV-1 addition. With an addition of 0.1 wt% CV-2, the bulk density of specimen sintered at 880°C for 2 h increased to 98.4 % of the theoretical density (7.35 g/cm³) of $BiNbO_4$ ceramic. Therefore, these results revealed that low-firing of $BiNbO_4$ was more easily to be achieved by the CV-2 addition.

Figure 3 illustrated the typical X-ray diffraction patterns of specimens doped with different contents of CV-1 or CV-2 sintered at 880°C for 2 h. These samples exhibited single orthorhombic $BiNbO_4$ phase without any second phase or impurity phase when either CV-1 or CV-2 was added. $BiNbO_4$ is known to have an orthorhombic-SbTaO₄ type crystal structure below 1020°C [16], and will transform to the triclinic phase at higher temperature. Therefore, the stable orthorhombic phase was obtained in the case of samples sintered at 880°C.

The SEM micrographs of $BiNbO_4$ ceramics with 0.3 wt.% CV-1 or CV-2 addition sintered at 880°C for 2 h are shown in Figure 4. The grain morphology of 0.3 wt.% CV-1-added $BiNbO_4$ ceramic is inhomogeneous and abnormal grain growth was observed, as is shown in Figure 4a. Moreover, lots of stick-shaped grains occurred with the addition of CV-1. It was reported that the abnormal grain growth and the stick-shaped grains were caused by the addition of V_2O_5 [16]. Therefore, the same condition was observed in the case of the sample doped with CuO- V_2O_5 mixtures. Figure 4b shows the SEM micrograph of 0.3 wt.% CV-2-added $BiNbO_4$ ceramic. The grain morphology is uniform. It was also observed that pores were almost eliminated with the

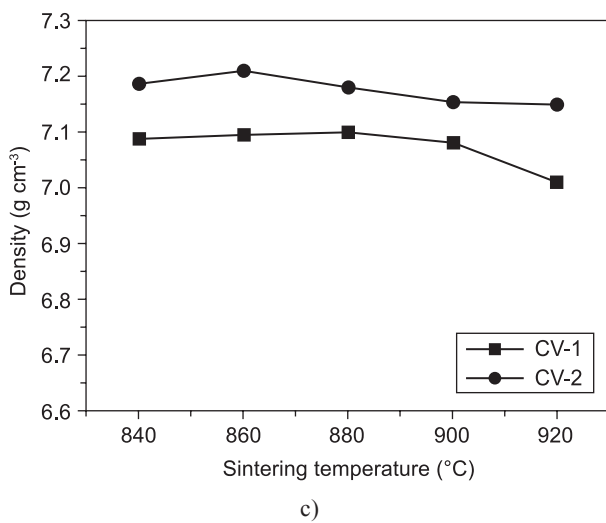
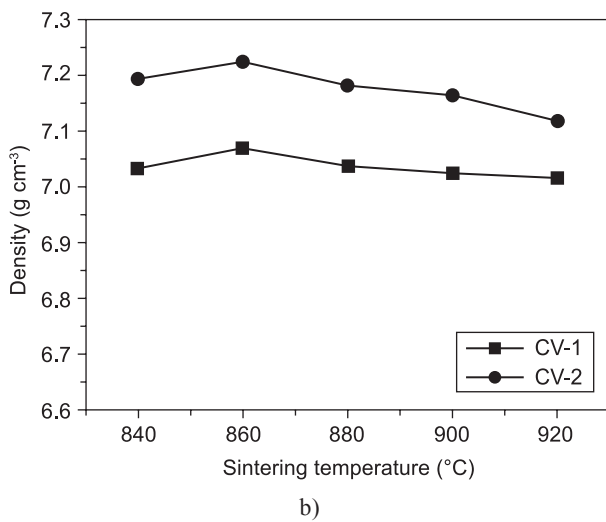
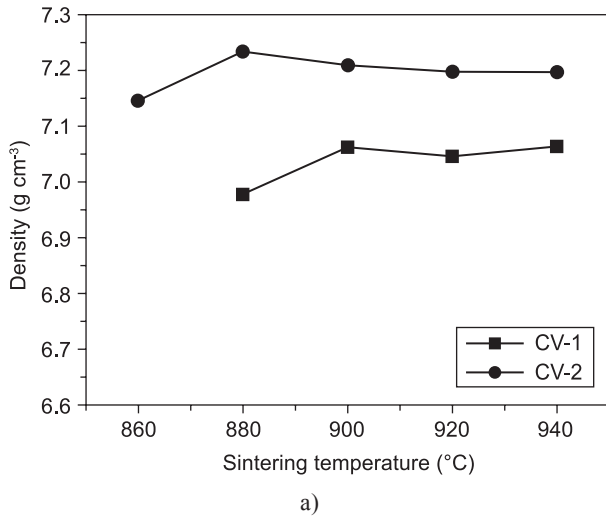


Figure 2. Bulk density of BiNbO₄ ceramics as functions of sintering temperature and the content of CuO–V₂O₅ complex; a) 0.1 wt%, b) 0.3 wt%, c) 0.5 wt%.

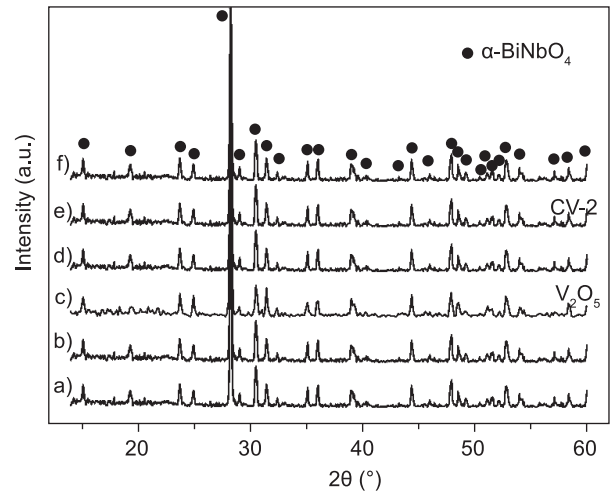


Figure 3. XRD patterns of BiNbO₄ ceramics sintered at 880°C with different CuO–V₂O₅ addition - a) 0.1 wt%, CV-1; b) 0.1 wt%, CV-2; c) 0.3 wt%, CV-1; d) 0.3 wt%, CV-2; e) 0.5 wt%, CV-1; f) 0.5 wt%, CV-2.

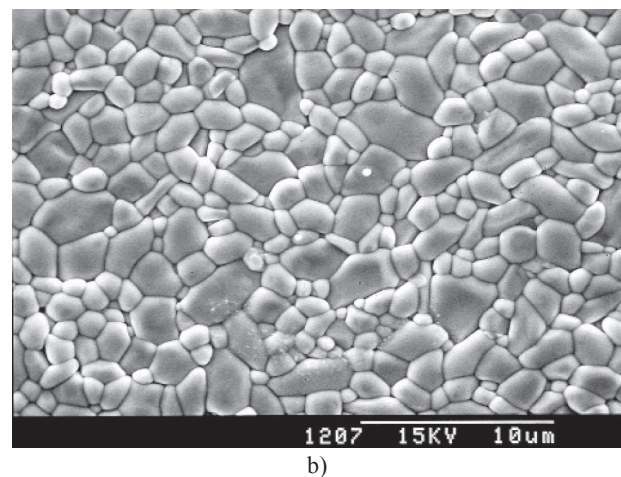
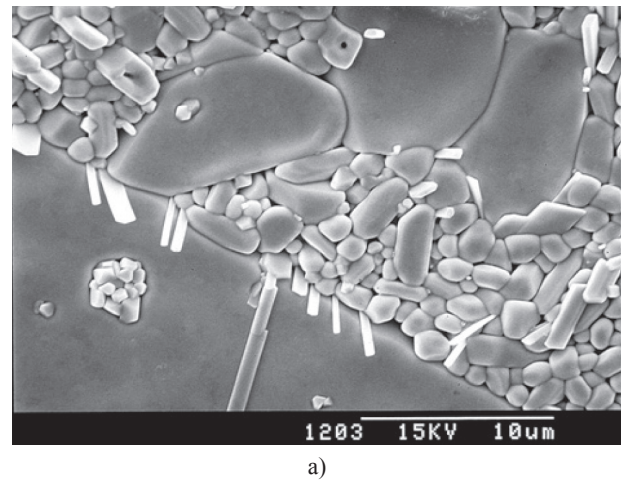


Figure 4. SEM micrographs of BiNbO₄ ceramics sintered at 880°C with 0.3 wt% - a) CV-1; b) CV-2.

addition of 0.3 wt.% CV-2, whereas many pores existed in grain boundary and triple point when 0.3 wt.% CV-1 was added. The same results were obtained as 0.5 wt.% CV-1 or CV-2 was doped (not presented here). In the case of CV-1 addition, CuO and V₂O₅ could not react totally and distribute uniformly in BiNbO₄ ceramics. However, when eutectic compound CuV₂O₆ was introduced to BiNbO₄ ceramics, homogeneous liquid phase was achieved during the sintering. Therefore, it was suggested that CuV₂O₆ addition was more favorable to lower the sintering temperature and improve the microstructure of BiNbO₄ ceramics.

The relative dielectric constant ϵ_r of 0.5 wt.% CV-1 or CV-2 added BiNbO₄ ceramics as a function of the sintering temperature is shown in Figure 5a. The ϵ_r of CV-2 added samples were higher than that of CV-1 added samples at the sintering temperatures ranged from 840 to 920°C, exhibiting the same trend as that of the bulk density since that dense ceramics have less pores (air,

$\epsilon = 1$) to deteriorate the ϵ value. Figure 5b shows the plots of the $Q \times f$ values (at 4.3 GHz) of 0.5 wt.% CV-1 or CV-2 doped BiNbO₄ ceramics versus sintering temperatures. The $Q \times f$ values of CV-2-doped BiNbO₄ ceramics were much higher than that for CV-1-doped samples. The

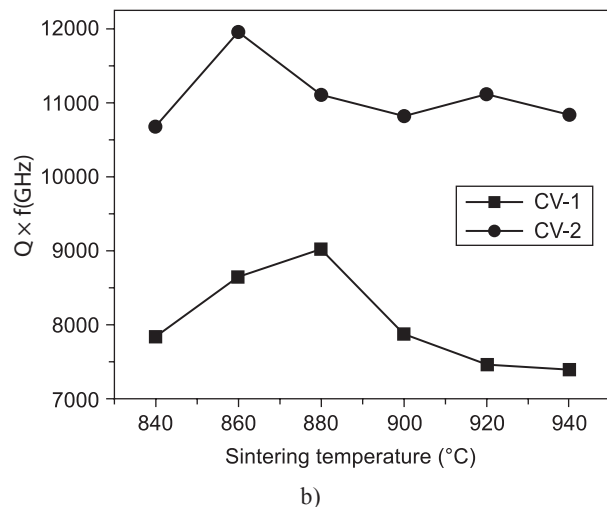
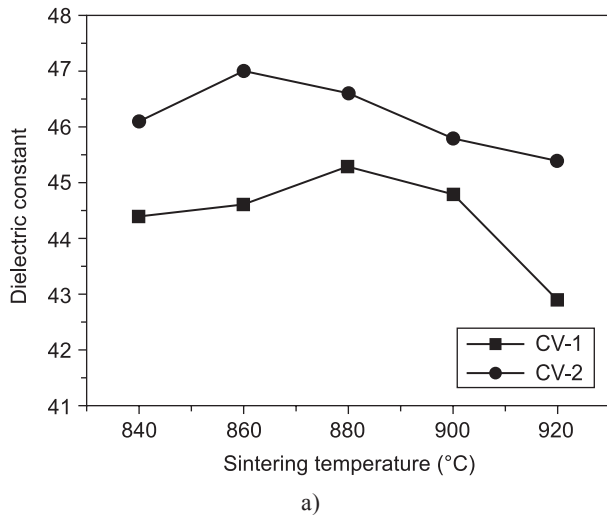
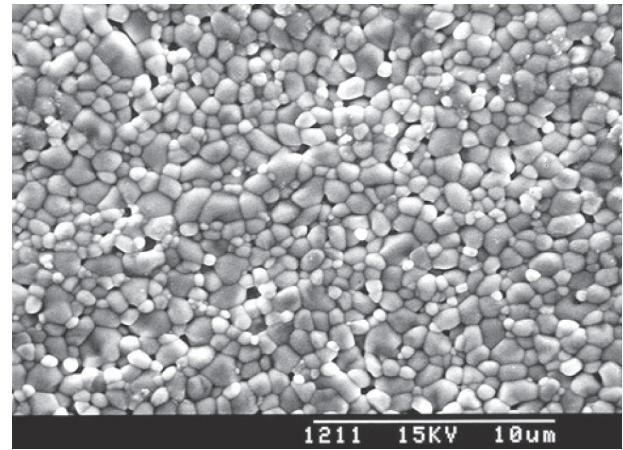
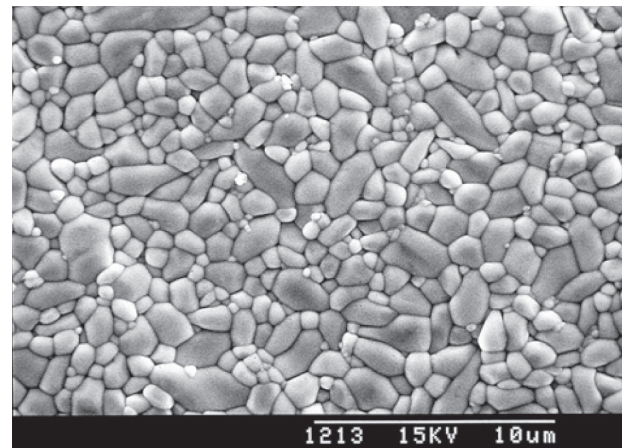


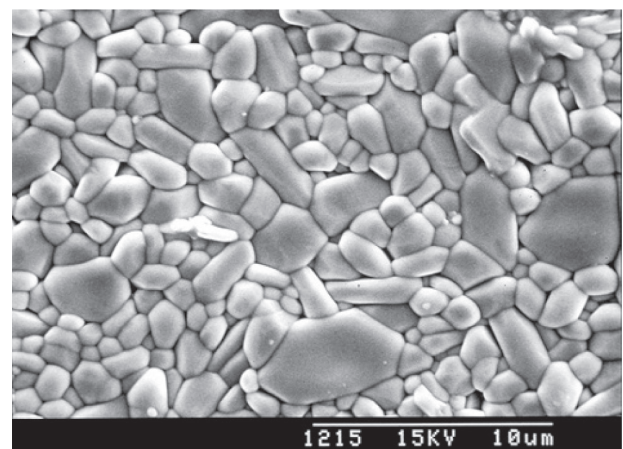
Figure 5. Microwave dielectric properties of BiNbO₄ ceramics with 0.5 wt.% CuO–V₂O₅ addition at different sintering temperature - a) dielectric constant, b) $Q \times f$ values.



a)



b)



c)

Figure 6. SEM micrographs of BiNbO₄ ceramics sintered at 860°C with different amounts of CV-2 - a) 0.1 wt.%; b) 0.3 wt.%; c) 0.5 wt.%.

maximum $Q \times f$ value 11950 GHz (at 4.3GHz) was obtained at the low sintering temperature of 860°C for 0.5 wt.% CV-2-doped BiNbO₄ ceramics. It is known that the loss of dielectric materials consists of intrinsic and extrinsic dielectric loss. The intrinsic dielectric loss is characteristic of the material, whereas extrinsic dielectric losses result from crystal defects, grain boundaries, second phases, pores etc. Thus, the increase of $Q \times f$ value was attributed to dense and homogeneous microstructure of CV-2 doped BiNbO₄ ceramics.

Figure 6 shows the effect of the content of CV-2 addition on the grain morphology of BiNbO₄ ceramics sintered at 860°C for 2 h. With an addition of 0.1 wt.% CV-2, BiNbO₄ ceramics were not dense and many grains did not grow. With 0.3 wt.% and 0.5 wt.% CV-2 additions, the pores were almost eliminated and the grain size increased with the content of CV-2. The grain growth was promoted by the liquid phase formed from the eutectic compound CuV₂O₆ during sintering as CV-2 was added to BiNbO₄. However, exaggerated grain growth was observed in the case of 0.5 wt.% CV-2 addition, resulting in the decrease in density. The observation implied that low-temperature sintering of BiNbO₄ ceramics could not be realized by insufficient amount of sintering aids, whereas exaggerating the amount of sintering aids resulted in a decrease in density.

CONCLUSION

It was found that the additions of CuO and V₂O₅ to BiNbO₄ ceramics can effectively reduce the sintering temperature. Compared with a simple mechanical mixture of CuO and V₂O₅, a compound of CuO and V₂O₅ (CuV₂O₆) was more effective in lowering the sintering temperature of BiNbO₄ ceramics. The addition of small amounts of CuV₂O₆ to BiNbO₄ enabled low-firing (98.4 % theoretical density) at approx 880°C. Pure orthorhombic BiNbO₄ phase was obtained successfully with the additions of either the CuO-V₂O₅ mixture or CuV₂O₆. The bulk densities, ϵ_r and $Q \times f$ values of BiNbO₄ ceramics with CuV₂O₆ addition were higher than those of the samples added with CuO-V₂O₅ mixture.

Inhomogeneous and exaggerated grain growth was observed in samples with the addition of CuO-V₂O₅ mixture while the uniform and dense microstructure was obtained in the case of CuV₂O₆ addition. BiNbO₄ ceramics sintered at 860°C for 2 h with 0.5 wt.% CuV₂O₆ addition have good microwave properties (at 4.3 GHz): $\epsilon_r = 47$ and $Q \times f = 11950$ GHz.

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References

1. Mhaisalkar S. G., Lee W. E., Readey D. W.: J. Am. Ceram. Soc. 72, 2154 (1989).
2. Henry M., O'Bryan, M., Thomson J.: J. Am. Ceram. Soc. 66, 66 (1983).
3. Huang C. L., Pan C. L., Shium S. J.: Mater. Chem. Phys. 78, 111 (2002).
4. Huang W., Liu K. S., Chu L. W.: J. Eur. Ceram. Soc. 23, 2559 (2003).
5. Kim D. W., Lee D. G., Hong K. S.: Mater. Res. Bull. 36, 585 (2001).
6. Chen C. S., Chou C. C., Chen C. S.: J. Eur. Ceram. Soc. 24, 1795 (2004).
7. Liu D. H., Liu Y., Huang S. Q.: J. Am. Ceram. Soc. 76, 2129 (1993).
8. Choy J. H., Han Y. S., Sohn J. H.: J. Am. Ceram. Soc. 78, 1169 (1995).
9. Kagata H., Inoue Y., Kato J.: Jpn. J. Appl. Phys. 31, 3152 (1992).
10. Ding S. H., Yao X., Yang Y.: Ceram. Int. 30, 1195 (2004).
11. Yang Y., Ding S. H., Yao X.: Ceram. Int. 30, 1335 (2004).
12. Wang Z. W., Yao X., Zhang L. Y.: Ceram. Int. 30, 1929 (2004).
13. Yang C. F.: Jpn. J. Appl. Phys. 38, 6797 (1999).
14. Yao Y., Zhao Y. M., Wang Y. L.: J. Inorg. Mater. 13, 176 (1998).
15. Fleury C. R. P.: Acad. Sci., Ser. C 263, 1375 (1966).
16. Keve E. T., Skapski A. C.: J. Sol. State Chem. 8, 159 (1973).