

Low-firing and microwave dielectric properties of $\text{Ba}[(\text{Ni}_{0.6}\text{Zn}_{0.4})_{0.33}\text{Nb}_{0.67}]\text{O}_3$ ceramics doped with Sb_2O_5 and B_2O_3

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The purpose of this study was to reduce the sintering temperature of $\text{Ba}[(\text{Ni}_{0.6}\text{Zn}_{0.4})_{0.33}\text{Nb}_{0.67}]\text{O}_3$ ceramics by doping with Sb_2O_5 and B_2O_3 . Phase formation and dielectric properties were analyzed using X-ray diffraction and the post resonator method (10 GHz), respectively. It was observed that an addition of 1 mol % Sb_2O_5 or 1 mol % B_2O_3 was very effective in reducing the sintering temperature from 1500 to 1300 °C. However, these samples showed a temperature coefficient of resonant frequency far from 0 ppm/°C. The two additions produced a temperature coefficients with opposite signs. The combination of the two dopants produced a temperature coefficient very close to 0 ppm/°C as well as a better quality factor. © 1999 Kluwer Academic Publishers

1. Introduction

In recent years special attention has been paid to dielectric materials used for microwave applications. These applications include dielectric resonators, various types of filters, microstrip antennas, and wave guides [1, 2]. The name microwave dielectric ceramics, was given to this group of materials. They include complex perovskite compounds, $(\text{Zr}, \text{Sn})\text{TiO}_4$, BaTi_4O_9 , $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ and $(\text{BaO}, \text{PbO})\text{-Nd}_2\text{O}_3\text{-TiO}_2$ [3–5].

The properties required for microwave dielectric ceramics are as follows: (i) Large permittivity, preferably larger than 15. (ii) Low dielectric loss which is associated with a high quality factor, Q . This parameter is usually represented by the Q^*F value, which is the product of quality factor and measuring frequency. This product is independent of frequency in the microwave region [1]. A Q^*F value greater than 5,000 is required although a much higher value is preferred in most applications. (iii) Small temperature coefficient of resonant frequency (τ_f). A τ_f value in the range of -5 to $+5$ ppm/°C is generally required. These three parameters with respect to the properties of microwave dielectrics are correlated to the size, frequency selectivity, and stability of a device, respectively.

In a previous work a new microwave dielectric composition based on the solid solution between $\text{Ba}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ and $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ was introduced [6]. Although this new composition has very promising dielectric properties, a relatively higher sintering temperature, 1500 °C, may limit its wide use. In contrast $(\text{Zr}, \text{Sn})\text{TiO}_4$ can be sintered at 1350 °C with the aid of ZnO as a sintering agent [7]. In the present work, reduced temperature sintering of $\text{Ba}[(\text{Ni}_{0.6}\text{Zn}_{0.4})_{0.33}\text{Nb}_{0.67}]\text{O}_3$ was attempted by doping with Sb_2O_5 and B_2O_3 .

2. Experimental procedure

$\text{Ba}[(\text{Ni}_{0.6}\text{Zn}_{0.4})_{0.33}\text{Nb}_{0.67}]\text{O}_3$ (abbreviated as BNZ) samples were prepared using the traditional mixed oxide method. Calcination was repeated twice to improve chemical homogeneity. High-purity raw materials (>99.9%, High Purity Chemical Co., Japan) of BaCO_3 , NiO, ZnO, and Nb_2O_5 were weighed and ball-milled for 1 h using a planetary mill. The slurry was dried and calcined in an alumina crucible at 1100 °C for 2 h. The calcined powders were ground and recalcined at 1100 °C for 2 h. Dopants of Sb_2O_5 and/or B_2O_3 were used. These dopants were mixed with the recalcined powder and then ball-milled for 24 h using zirconia media and distilled water. The slurry was then dried in an electric oven at 100 °C. The dried powder was uniaxially pressed into pellets 1 cm in diameter and 4 ~ 5 mm thick using 1000 kg/cm² pressure. Pellets were sintered in the temperature range of 1300 to 1400 °C for 2 h with heating rate of 5 °C/min and followed by cooling of 5 °C/min. Designations of samples with respect to dopant and amount are listed in Table I.

Sintered samples were analyzed by X-ray diffraction (Rigaku, Model D/max-3c, Japan). Bulk densities of the sintered samples were measured using the Archimedes method. Dielectric properties of samples were measured at 10 GHz by the post resonator method using a network analyzer (Hewlett Packard, Model HP 8510B, USA).

3. Results and discussion

3.1. Effects of Sb_2O_5 addition

Fig. 1 shows the bulk densities of BNZS samples as a function of the amounts of Sb_2O_5 dopants. The

TABLE I Designations of samples with dopants

Dopant	0.5 mol %	1.0 mol %	2.0 mol %	3.0 mol %	4.0 mol %	5.0 mol %
Sb ₂ O ₅	BNZS0.5	BNZS1.0	BNZS2.0	BNZS3.0	BNZS4.0	BNZS5.0
B ₂ O ₃	BNZB0.5	BNZB1.0	BNZB2.0	—	—	—
0.5 mol % Sb ₂ O ₅ + x mol % B ₂ O ₃	BNZC0.5	BNZC1.0	BNZC2.0	—	—	—

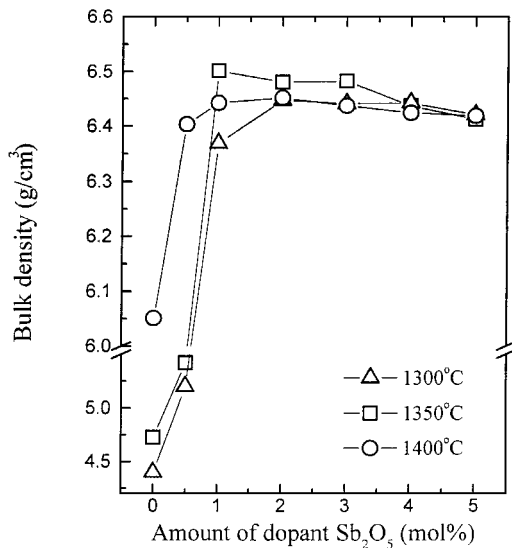


Figure 1 Bulk densities of BNZS samples as a function of the amount of Sb₂O₅ dopant with various sintering temperatures.

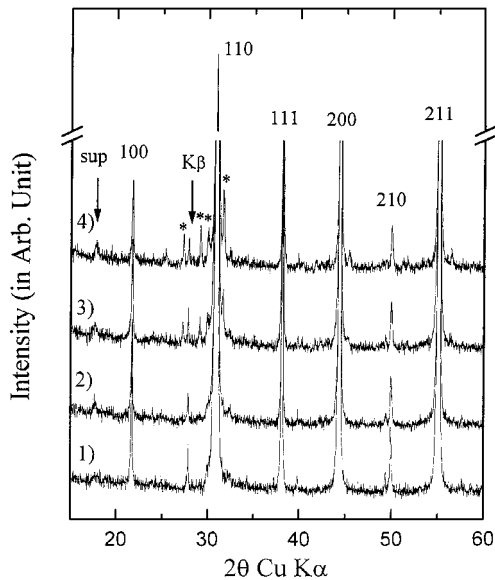


Figure 2 XRD patterns of BNZS samples sintered at 1300 °C: 1) BNZS0.5, 2) BNZS1.0, 3) BNZS3.0, 4) BNZS5.0. (indices are based on simple cubic perovskite, “sup” means superlattice reflection of 1:2 ordering, “*” means reflections due to second phases)

densities are also shown at three different sintering temperatures. In this figure it is obvious that the addition of Sb₂O₅ more than 1 mol % enhances the sinterability of BNZ samples producing dense samples.

Fig. 2 shows XRD patterns of BNZS samples sintered at 1300 °C with various amount of dopant (0.5, 1.0, 3.0, 5.0 mol %). All samples revealed reflections primarily attributed to a perovskite phase. However, only the BNZS0.5 sample had a disordered structure while the other samples exhibited an ordered structure.

This variation in order-disorder behavior observed in the BNZS0.5 sample may be attributed to its lower density. Density can be linked to cation ordering on the B-site which is dependent on the interdiffusion of the cations. A lower density therefore represents insufficient mass transport and subsequent interdiffusion. The lattice parameter of the BNZS0.5 sample was calculated to be 4.041 Å using the 2θ of the (110) reflection, shown in Fig. 2, since this sample had a cubic perovskite unit cell. The theoretical density of BNZ samples was calculated from crystallographic data to be 6.605 g/cm³. By applying this theoretical density to the bulk densities shown in Fig. 1, the porosities of the BNZS0.5 and BNZS1.0 samples sintered at 1300 °C were estimated as 20.1 and 2.1%, respectively.

Fig. 3 shows the relative permittivity of BNZS samples as a function of amount of Sb₂O₅ dopants with variations in sintering temperature. Measured permittivity of samples was corrected for their porosity using the following relation,

$$\epsilon_{\text{corrected}} = \epsilon_{\text{measured}} / (1 + 0.5P)$$

(where $P \times 100 = \% \text{ porosity}$) [8]. Comparison of Fig. 3 to Fig. 1 revealed that a sharp increase in permittivity in the range of 0 to 1.0 mol % of Sb₂O₅ was due to an increase in sintered density. While the bulk density reached its maximum value at above 1.0 mol % dopant, the permittivity continued to increase slowly. This slow increase in permittivity above 1.0 mol % of Sb₂O₅ may be attributed to the formation of a second phase with

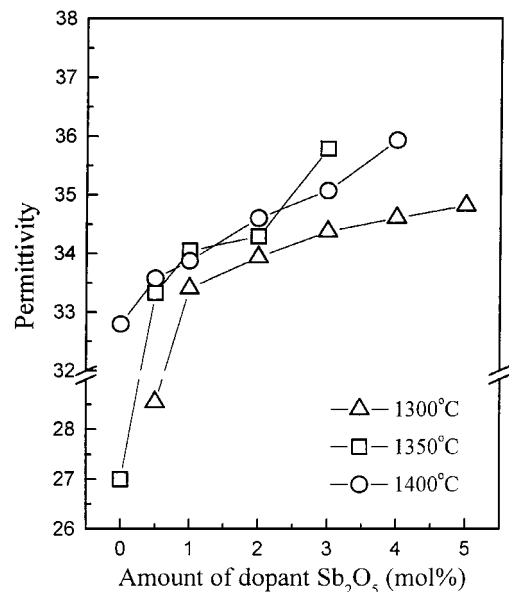


Figure 3 Permittivity of BNZS samples as a function of the amount of Sb₂O₅ dopant with various sintering temperatures.

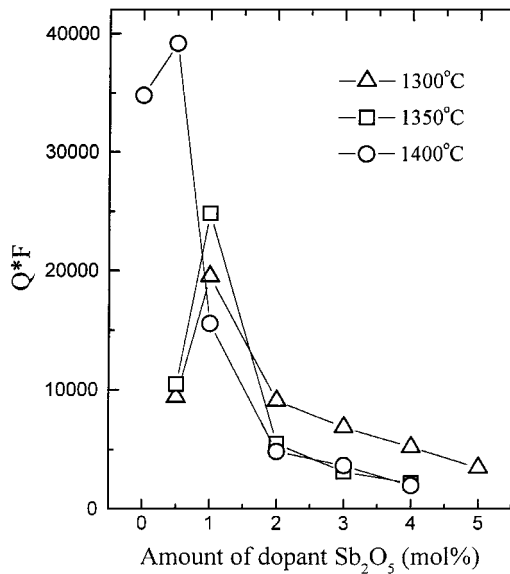


Figure 4 Quality factor of BNZS samples as a function of the amount of Sb_2O_5 dopant with various sintering temperatures.

increasing amount of dopant. In Fig. 2 the BNZS3.0 and BNZS5.0 samples had many reflections arising from a second phase whereas the BNZS0.5 and BNZS1.0 samples did not exhibit the presence of a second phase.

Fig. 4 shows the quality factors of BNZS samples as a function of amount of Sb_2O_5 dopant with variation in sintering temperature. Although a small amount of doping increases the quality factor ($Q \cdot F$) of BNZ (for example, from 35,000 of undoped BNZ to 40,000 of BNZS0.5 sintered at 1400°C) due to increase in sintering density, in this figure a drastic decrease in quality factor with further increasing amount of dopant is obvious. The quality factor of undoped BNZ sintered at 1400°C is approximately 35,000, while the BNZS1.0 sample sintered at 1300°C had a quality factor of 20,000. This result indicates that the addition of Sb_2O_5 has a serious disadvantage with respect to properties although it is very useful to achieve low-firing.

3.2. Effects of B_2O_3 addition

Table III lists bulk densities and microwave dielectric properties of sintered BNZ samples with various amounts of B_2O_3 dopant (BNZB samples). Here it is evident that the addition of B_2O_3 was also very effective in enhancing the sinterability of BNZ ceramics. The BNZB1.0 samples had higher bulk densities in comparison to the BNZS1.0 samples. In Table III the permittivity of BNZB samples showed a slight decrease with increasing amount of B_2O_3 , unlike the BNZS samples. Similarly BNZS samples and BNZB samples also showed a decrease in quality factor with increasing amounts of B_2O_3 dopant. Tables II and III indicate that with increasing amounts of dopants BNZS and BNZB samples exhibited opposite changes in τ_f , with respect to $0 \text{ ppm}/^\circ\text{C}$.; BNZS samples had increased $\tau_f (>0)$ in comparison to BNZ samples while BNZB samples decreased ($\tau_f < 0$).

Fig. 5 shows the XRD patterns of BNZB samples sintered at 1350°C . Comparing the XRD patterns of BNZS samples (Fig. 2) revealed that the addition of B_2O_3 was

TABLE II Temperature coefficient of resonant frequency of BNZS samples

Sample	BNZ	BNZS0.5	BNS1.0	BNZS3.0
Sintering Temperature ($^\circ\text{C}$)	1525	1350	1350	1350
τ_f (ppm/ $^\circ\text{C}$)	3.0	-2.0	1.9	13.8

TABLE III Bulk densities and dielectric properties of BNZB samples

Sample	Sintering temperature	Bulk density (g/cm^3)	ϵ_r	$Q \cdot F$	τ_f (ppm/ $^\circ\text{C}$)
BNZB0.5	1300°C	6.43	34.2	36700	-2.7
	1350°C	6.46	34.3	42100	-5.7
BNZB1.0	1300°C	6.45	33.2	39700	-4.2
	1350°C	6.47	33.7	30100	-11.2
BNZB2.0	1300°C	6.31	32.9	32500	-10.7
	1350°C	6.33	33.0	27400	-15.6

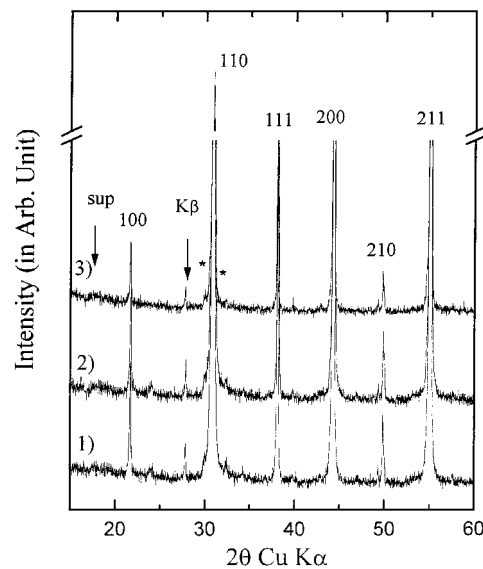


Figure 5 XRD patterns of BNZB samples sintered at 1300°C : 1) BNZB0.5, 2) BNZB1.0, 3) BNZB2.0 (indices are based on simple cubic perovskite, "sup" means superlattice reflection of 1:2 ordering, "*" means reflections due to second phases).

not associated with the formation of a second phase. This result implies that B_2O_3 may be incorporated into the perovskite lattice. In Fig. 5 it is also noteworthy to add that B_2O_3 doping favors a disordered structure. This behavior explains the decrease in τ_f , since τ_f can be changed by crystal structure of specimen depending on long range cation ordering [9].

3.3. Combination of dopants

In previous sections it was evident that both Sb_2O_5 and B_2O_3 were very useful in enhancing the sinterability of BNZ by lowering the sintering temperature. However, the quality factor showed a sharp decrease and τ_f showed a large deviation from $0 \text{ ppm}/^\circ\text{C}$ with increasing amounts of dopant. The opposite effects of dopants on τ_f demonstrated by BNZS and BNZB samples implies that a combination of Sb_2O_5 and B_2O_3 (BNZC samples) may produce a small temperature coefficient

of resonant frequency. Since the decrease in quality factor was more abrupt in BNZS samples, the amount of Sb_2O_5 doped was chosen as 0.5 mol %.

Fig. 6 shows bulk densities and permittivity of BNZC samples as a function of the amount of B_2O_3 dopant. As expected, the combination of dopants was very effective to enhance the sinterability and to achieve a high permittivity. Fig. 7 shows the quality factor and τ_f of BNZC samples as a function of the amount of B_2O_3 dopant. Here quality factor of the BNZC1.0 sample had a maximum value of 43,000, which is higher than the value obtained using either Sb_2O_5 or B_2O_3 alone. In Fig. 7 the optimization of τ_f is clear; both the BNZC0.5 and BNZC1.0 sample had τ_f values close to 0 ppm/°C. This result indicates that the effect of Sb_2O_5 and B_2O_3 on τ_f was to counteract each other through co-doping. It is striking to note, however, that the increase in the amount of B_2O_3 was accompanied by a positive deviation of τ_f in comparison to the BNZ sample; while an opposite deviation of τ_f may arise from the co-doping. The effect of doping on crystal structure, and in turn, τ_f of

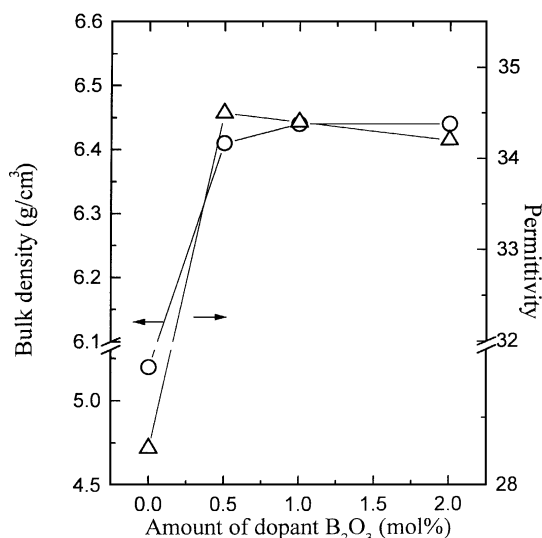


Figure 6 Bulk density and permittivity of BNZC samples sintered at 1300 °C as a function of the amount of B_2O_3 dopant.

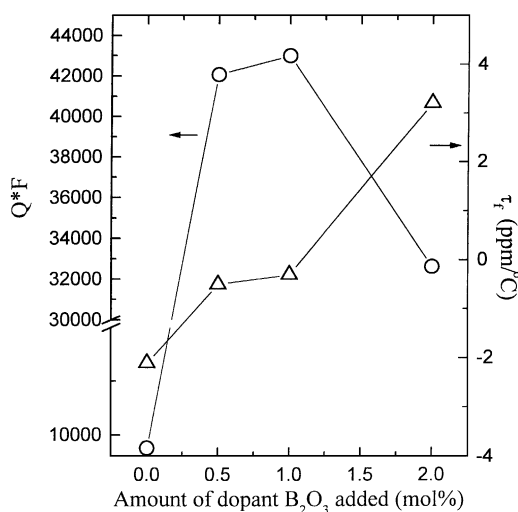


Figure 7 Quality factor and temperature coefficient of resonant frequency of BNZC samples sintered at 1300 °C as a function of the amount of B_2O_3 dopant.

specimen may be very complex in the case of co-doping and should be studied further to discern its origin.

In Figs 6 and 7 the BNZC1.0 sample doped with 0.5 mol % Sb_2O_5 and 1.0 mol % B_2O_3 exhibited the following dielectric properties: permittivity 34.5, Q^*F value 43000, and $\tau_f - 0.3$ ppm/°C. In a previous work [6], a $\text{Ba}[(\text{Ni}_{0.6}\text{Zn}_{0.4})_{0.33}\text{Nb}_{0.67}]\text{O}_3$ sample prepared by the Pechini method and sintered at 1500 °C for 2 h showed dielectric properties as follows: permittivity 35.6, Q^*F value 57440, and $\tau_f - 0.5$ ppm/°C. Although the use of dopants slightly lowered the permittivity and quality factor, this result revealed that the low-firing of BNZ produced samples with useful properties.

4. Conclusions

(1) Doping with Sb_2O_5 in $\text{Ba}[(\text{Ni}_{0.6}\text{Zn}_{0.4})_{0.33}\text{Nb}_{0.67}]\text{O}_3$ (BNZ) system was very effective in enhancing the sinterability. The sintering temperature was reduced to 1300 °C with 1.0 mol % dopant, which is 200 °C lower than the BNZ sintering temperature (1500 °C). However, the quality factor showed an abrupt decrease with increased doping. Variation in dielectric properties with increased doping was ascribed to the formation of a second phase.

(2) Doping with B_2O_3 in BNZ was also found to be very effective in enhancing the sinterability. Sintering temperature and dielectric properties of BNZB samples with 1.0 mol % dopant were comparable to the BNZS sample doped with 1.0 mol % Sb_2O_5 . Dielectric properties also showed a degradation with increased amounts of dopant but this was ascribed to the incorporation of B_2O_3 in the perovskite lattice.

(3) An opposite deviation of τ_f demonstrated by the samples doped with Sb_2O_5 and B_2O_3 led us to choose a dopant combination, i.e. 0.5 mol % $\text{Sb}_2\text{O}_5 + x$ mol % B_2O_3 . Compared to the samples doped with either Sb_2O_5 or B_2O_3 alone, the co-doped samples showed improved dielectric properties, notably a τ_f value close to 0 ppm/°C. The sample with 1.0 mol % B_2O_3 , which was sintered at 1300 °C, revealed the best dielectric properties: permittivity 34.5, Q^*F value 43000, and $\tau_f - 0.3$ ppm/°C.

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