Microwave dielectric properties of Ba(Co$_{0.47+x}$Y$_{0.04}$Zn$_{0.35}$)$_{1/3}$Nb$_{2/3}$O$_3$ ($x = 0–0.13$) ceramics

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The sintering behaviors and microwave dielectric properties of Ba(Co$_{0.47+x}$Y$_{0.04}$Zn$_{0.35}$)$_{1/3}$Nb$_{2/3}$O$_3$ ($x = 0–0.13$) ceramics were investigated in this paper. The XRD results showed all samples exhibited the main phase Ba(Co$_1/2$Nb$_1/2$)O$_3$–Ba(Zn$_1/2$Nb$_1/2$)O$_3$ (BCZN) and a certain amount of secondary phase Ba(Nb$_2$O$_5$). SEM revealed that the microstructure was homogeneous fine grained when $x$ equaled to 0.13. The Co deficiency was found unfavorable to improve the microwave dielectric properties of BCZN ceramics and showed remarkable influence on crystal phases and microstructures. The relatively optimized microwave dielectric properties could be obtained when Co was adequate. At last, the Ba(Co$_{0.47+x}$Y$_{0.04}$Zn$_{0.35}$)$_{1/3}$Nb$_{2/3}$O$_3$ ceramics well-sintered at 1340°C for 20 h had good microwave dielectric properties of $\varepsilon_r = 35.0$, $Q\times f = 44,833$ GHz and $\tau_r = -1.1$ ppm/°C.

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compositions in our ceramic systems. Figure 1 depicted the XRD patterns of Ba(Co0.56Y0.04Zn0.35)1−x/3Nb2/3+yO3−x powders with different x value calcined at 1150°C for 3 h were illustrated in Fig. 2. For the calcined sample with the composition of x = 0, it showed the lowest peak intensity of BCZN phase. It was apparent that there was only BCZN main phase and no other impurity phase appeared with increasing x in BCYZN powders. Figure 3(a) showed the XRD patterns of BCYZN ceramics with different x value sintered at 1340°C for 20 h. It was notable that besides the same crystal main phase of BCZN, a certain amount of Ba5Nb4O15 secondary phase was found in all samples. Moreover, a small amount of unknown phase was observed at the composition of x = 0.13. From the graph we also could see that the amount of main crystal phase increased slightly as x value was changed from 0 to 0.13. Especially for the composition of x = 0.13, the XRD pattern of the main crystal phase showed the strongest peak intensity. The XRD patterns for the Ba5Nb4O15 secondary phase of the same specimens were shown in Fig. 3(b), from which we could see that peak intensity of Ba5Nb4O15 decreased with increasing x value. Obviously, compared to other compositions, there was the smallest amount of Ba5Nb4O15 phase with x = 0.13 in BCYZN ceramics. As reported in previous researches, the hexagonal Ba5Nb4O15 phase commonly appeared in BCZN ceramics even for the stoichiometric BCN or BZN system. Although the occurrence of Ba5Nb4O15 always had a negative effect on the microwave dielectric properties, the XRD results shown in Figs. 3(a) and 3(b) demonstrated that the Ba5Nb4O15 secondary phase definitely existed in the sintered ceramics. However, Ba5Nb4O15 phase was not presented in the calcined powders. The probable reason for this discrepancy between Figs. 2 and 3 was that the calcining temperature of 1150°C was too low for the starting powders to form Ba5Nb4O15 phase. As it has conclusively been shown that the lowest temperature for the formation of Ba5Nb4O15 phase was 1200°C and the sintering temperature of Ba5Nb4O15 ceramics was above 1400°C.

With careful observation of Fig. 3(a), it was found that there was a movement of the peaks towards higher degrees for BCYZN. Hence the lattice parameters and c/a ratio for the BCYZN phase were calculated and the results were shown in Fig. 3. Results and discussions

The XRD patterns for Ba(Co0.47+44Y0.04Zn0.35)1−x/3Nb2/3+yO3−x powders with different x value calcined at 1150°C for 3 h were illustrated in Fig. 2. For the calcined sample with the composition of x = 0, it showed the lowest peak intensity of BCZN phase. It was apparent that there was only BCZN main phase and no other impurity phase appeared with increasing x in BCYZN powders. Figure 3(a) showed the XRD patterns of BCYZN ceramics with different x value sintered at 1340°C for 20 h. It was notable that besides the same crystal main phase of BCZN, a certain amount of Ba5Nb4O15 secondary phase was found in all samples. Moreover, a small amount of unknown phase was observed at the composition of x = 0.13. From the graph we also could see that the amount of main crystal phase increased slightly as x value was changed from 0 to 0.13. Especially for the composition of x = 0.13, the XRD pattern of the main crystal phase showed the strongest peak intensity. The XRD patterns for the Ba5Nb4O15 secondary phase of the same specimens were shown in Fig. 3(b), from which we could see that peak intensity of Ba5Nb4O15 decreased with increasing x value. Obviously, compared to other compositions, there was the smallest amount of Ba5Nb4O15 phase with x = 0.13 in BCYZN ceramics. As reported in previous researches, the hexagonal Ba5Nb4O15 phase commonly appeared in BCZN ceramics even for the stoichiometric BCN or BZN system. Although the occurrence of Ba5Nb4O15 always had a negative effect on the microwave dielectric properties, the XRD results shown in Figs. 3(a) and 3(b) demonstrated that the Ba5Nb4O15 secondary phase definitely existed in the sintered ceramics. However, Ba5Nb4O15 phase was not presented in the calcined powders. The probable reason for this discrepancy between Figs. 2 and 3 was that the calcining temperature of 1150°C was too low for the starting powders to form Ba5Nb4O15 phase. As it has conclusively been shown that the lowest temperature for the formation of Ba5Nb4O15 phase was 1200°C and the sintering temperature of Ba5Nb4O15 ceramics was above 1400°C.

With careful observation of Fig. 3(a), it was found that there was a movement of the peaks towards higher degrees for BCYZN. Hence the lattice parameters and c/a ratio for the BCYZN phase were calculated and the results were shown in
Fig. 4. Viewed overall, the value of c/a ratio kept an upward trend with the increasing x value, although it presented abnormal changes at the composition of x = 0.03 and 0.06. And the most important indicator of the trigonal distortion caused by the cation ordering is the c/a ratio in the BCZN ceramics. Therefore, our results implied that to some extent the c/a ratio value could be raised with increasing x.

The SEM micrographs for Ba(Co_{0.47}+xY_{0.04}Zn_{0.35})_{1/3-Nb_{2/3}O_{0.05}} ceramic samples sintered at 1340°C for 20 h were presented in Fig. 5. It could be seen that there was a large amount of pores on the surface of ceramics when x ≤ 0.09. While increasing x, the grain size of BCYZN ceramics did not change apparently, but the porosity decreased remarkably. Not only did the ceramic porosity went down to the smallest level, but the densification improved greatly and the grain size became uniform as well at the composition of x = 0.13. As reported by Wu et al., the grain size of BN ceramics was about 1–3 μm and it would even go up to 5–8 μm via liquid phase sintering mechanism. Bian et al. studied that the grain size of Ba-deficient specimens were larger than that of Ba-excessive samples and it was likely that the Ba-deficiency promoted the growth of grain size. However, we found that Co-site deficiency had an influence on the dense growth, whereas it did not result in the variation of grain size in this investigation, which was different from the studies of former counterparts.

Figure 6 displayed the variation of apparent density for Ba(Co_{0.47}+xY_{0.04}Zn_{0.35})_{1/3-Nb_{2/3}O_{0.05}} ceramic samples sintered at different temperature as function of different x value. For x varying from 0.00 to 0.06, the apparent density of samples with each fixed x value showed an increasing trend with sintering temperature increased up to 1420°C. Moreover, we found that specimens with large amounts of Co deficiency (x = 0.06) needed to be sintered well at a relatively high temperature of more than 1400°C. The apparent densities of samples with x = 0.13 sintered at 1340 and 1380°C were larger than that of other compositions. It could be seen that the density of BCYZN ceramics reached the maximum value of 6.41 g/cm³ with x equaled to 0.13 at 1340 and 1380°C were larger than that of other compositions. It could be seen that the density of BCYZN ceramics reached the maximum value of 6.41 g/cm³ with x equaled to 0.13 at 1340°C, consequently the sintering temperature decreased with increasing x value. Because the theoretical densities of both secondary phase (Ba_{3}Nb_{2}O_{15} = 6.34 g/cm³,
Fig. 6. Apparent density of Ba(Co0.47+δ,Y0.05Zn0.35)1-x/Nb2/3-xO3 ceramics sintered at different temperature as a function of different x value.

Fig. 7. Dielectric constant of Ba(Co0.47+δ,Y0.05Zn0.35)1-x/Nb2/3-xO3 ceramics sintered at different temperature as a function of different x value.

Fig. 8. Q×f value of Ba(Co0.47+δ,Y0.05Zn0.35)1-x/Nb2/3-xO3 ceramics sintered at different temperature as a function of different x value.

JCPDS Card No. 01-087-1248 and pores (density ≈0) were lower than that of BCN phase (6.50 g/cm³, JCPDS Card No. 00-046-0097) and BZN phase (6.63 g/cm³, JCPDS Card No. 01-089-3115), the declination of Ba2Nb3O8 phase and pores caused the improvement of the apparent density with increasing x value. Previous research revealed that the Ba deficiency in the BCZN ceramics resulted in the decrease of porosity and increase of apparent density, whereas we found it was extremely difficult for the BCYZN ceramics to be well-sintered when the Co site was deficient. Yue et al. reported that the sintering temperature of BCZN ceramics was generally higher than 1400°C. Also, another study suggested that BCZN specimens could not be sintered to high density even though the sintering temperature was higher than 1425°C under thermal insulation condition for 10 h. Therefore, when comparing our results with previous studies, we could clearly see that the B-site nonstoichiometry and Y2O3 modification would reduce the sintering temperature for more than 50°C in BCZN ceramic systems.

Figure 7 showed the variation of dielectric constant for Ba(Co0.47+δ,Y0.05Zn0.35)1-x/Nb2/3-xO3 ceramic samples sintered at different temperature as function of different x value. For the fixed x value, the variation of dielectric constant shown in Fig. 5 was almost agreement well with that of apparent density presented in Fig. 6. Our results indicated that high dense samples with low levels of Ba5Nb4O15 impurity phase tended to exhibit high dielectric constant for BCYZN ceramics. The possible reason was that both the dielectric constant and apparent density were affected by densification process and phase constituent. As seen from Fig. 5, the dielectric constant values were strongly dependent on the sintering temperature. At the composition of x ≤ 0.06, the dielectric constant increased obviously with increasing sintering temperature due to the large amounts of Co deficiency and relatively high sintering temperature. As we know, the dielectric constant was strongly influenced by densities and pores(εr = 1). Therefore, it was reasonable to understand the εr value of the ceramics sintered at 1340°C for 20 h increased sharply from 31.1 to 35.0 as x was changed from 0 to 0.13. Although the Ba5Nb4O15 possessed relatively high dielectric constant of 41.0, our results indicated that the small amount of impurity phase failed to affect the dielectric constant.

The variation of Ω×f values for Ba(Co0.47+δ,Y0.05Zn0.35)1-x/Nb2/3-xO3 ceramic samples sintered at different temperature as a function of different x value were presented in Fig. 8, from which we could see that they all display an increasing trend when x ≤ 0.06. At the composition of 0.09 ≤ x ≤ 0.13, it reached its maximum value at sintering temperature of 1340°C then started to decline. As discussed before, the Ω×f value was affected by many factors, such as 1:2 long-range ordering, lattice distortion (c/a), structure defects, densification, impurity phases, micro-morphology and grain size, so sometimes it was difficult to determine the key influencing factors. However, in our case the predominant influential factors of the Ω×f value were quite clear. First of all, it was reported that an improvement of the Ω×f value in Ba(Zn3/2Nb1)O3 was accompanied by an increase in the c/a ratio. Let us associate Fig. 4 with Fig. 8, the increase of c/a ratio may contribute to improvement of Ω×f value when x was raised from 0 to 0.13. More importantly, it is reasonably believed that these changes in BCYZN ceramics were related to the samples' compactness, that is to say, the denser the microstructure, the higher the Ω×f value. Moreover, the decreasing amount of Ba5Nb4O15 impurity phase contributed to the Ω×f value to some extent. The relatively lower Ω×f value of Ba2Nb3O15 (26,337 GHz) was considered to be partially responsible for the improvement of the Ω×f value, when compared with pure BCN and BZN which had Ω×f value about 100,000 and 90,000 GHz, respectively. Hence, when increasing the x value, the Ω×f value of the sintered BCYZN ceramics increased owning to the
improvement of densification and declination of impurity phase. From another point of view, the evaporation of ZnO and CoO was inevitable for zinc and cobalt containing ceramics during sintering at high temperature. Consequently, the structure defects in perovskite lattice may be formed due to the loss of Zn and Co, which could result in the decreasing of Q×f value at high sintering temperature when 0.09 ≤ x ≤ 0.13.

The temperature coefficient of resonant frequency (τr) of Ba(Co0.47-xY0.04Zn0.35)1/3Nb2/3-3xO3 ceramic samples with different x value were shown in Fig. 9, from which it was found that as x was increased from 0 to 0.20, the τr values varied gradually toward negative direction from 8.5 to −1.1 ppm/°C. A considerable amount of literature has been published on temperature coefficient of resonant frequency for BCZN ceramics and this ceramic system always showed a near zero τr value.3,23 When it came to other elements doped BCZN ceramics, several studies have revealed that the variation of τr as a function of doping amount often exhibited an increasing trend in previous articles.3,10 However, for nonstoichiometric BCZN ceramics, it has been suggested that the τr values in accordance with the levels of Co-deficient presented a decreasing trend owing to the multi-phase composition.11 As is well known, the τr value is mainly related to the composition, the additive and the second phase of a material. The τr value of samples were declined with increasing x value due to the decreasing of Ba3Nb2O15 secondary phase as indicated by Fig. 2(b), which possessed a large positive τr of +78 ppm/°C.31 The present findings seemed to be consistent with previous research which found less Co-deficient could achieve low τr values in BCZN ceramics.11 It also demonstrated a transition of τr value from positive to negative as the x varied from 0 to 0.13. This implies that zero τr could be obtained by appropriately adjusting the amount of Co-deficient.

In summary, the Co deficiency in Ba(Co0.47+xY0.04Zn0.35)1/3Nb2/3-3xO3 system was unfavorable to improve the microwave dielectric properties. It was always accompanied by the formation of impurity phase and resulted in the increase of sintering temperature. Typically, Ba(Co0.60Y0.02Zn0.33)1/3Nb2/3-3xO3 ceramic sintered at 1340°C exhibited relatively dense microstructure and good microwave dielectric properties of εr = 35.0, Q×f = 44,833 GHz and τr = −1.1 ppm/°C. In addition to a slightly lower sintering temperature, BCYZN ceramics prepared by B'-site nonstoichiometry and doping modification exhibited better microwave dielectric properties compared with that of non-doped BCZN ceramics sintered at 1425°C29 (εr = 35.8, Q×f = 30,426 GHz and τr = 8.2 ppm/°C).

4. Conclusions

The effects of Co deficiency on the phase structures, sintering behaviors and microwave dielectric properties of Ba(Co0.47-xY0.04Zn0.35)1/3Nb2/3-3xO3 ceramics were investigated on the basis of B'-site nonstoichiometry and doping modification of Y2O3. As x was increased from 0.00 to 0.13, XRD analysis revealed the amount of main phase (BCZN) increased, meanwhile, that of Ba3Nb2O15 secondary phase decreased sharply. A similar trend was observed between the apparent density and εr value. When the Co content was deficient (x ≤ 0.06), the εr value increased obviously with increasing sintering temperature due to the improvement of densification. Typically, when the Co atoms were sufficient (x = 0.13), a high εr value for ceramic sintered at 1340°C for 20h of 35.0 was obtained, and the Q×f value first increased from 34,713 to 44,833 GHz, thereafter it declined to 37,942 GHz. Our results indicated that the Q×f value was strongly affected by densification as well as secondary phase. The τr value linearly decreased as x value increased. Hence, our specimens with composition of Ba(Co0.47-xY0.04Zn0.35)1/3Nb2/3-3xO3 sintered at 1340°C for 20h showed good microwave dielectric properties of εr = 35.0, Q×f = 44,833 GHz and τr = −1.1 ppm/°C.

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