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Mn^{4+} and W^{6+} substitution on Bi_2O_3–ZnO–Nb_2O_5-based low firing ceramics

Hong Wang*, Zhen Peng, Huiling Du, Tingwei Yao, Xi Yao

Electronic Materials Research Laboratory, Key Laboratory of Education Ministry, Xi'an Jiaotong University, Xi'an 710049, China

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Abstract

The ion substitution with Mn^{4+} and W^{6+} co-substituted Nb^{5+} in B site of a low firing Bi_2O_3–ZnO–Nb_2O_5-based $A_2B_2O_7$ pyrochlore ceramics was investigated. The Mn^{4+} and W^{6+} co-substitution was tentatively introduced in cubic-monoclinic pyrochlores co-existing ceramics $Bi_{3x}Zn_{2-3x}(Zn_xNb_{2-x-2y}Mn_yW_y)O_7$ ($x = 0.5$–0.65, $y = 0, 0.02, 0.05, 0.1$) and the results shows interested regular influence on the structure, dielectric properties with the amount of substitution amount change. With the structure evaluation and electrical properties measurement results, the Mn^{4+} and W^{6+} substituted Nb^{5+} in B site shows effective to depress the grain growth and the ceramic with fine grains in 1–3 μm can be obtained. The electrical properties was also enhanced in smaller substitution amount but degraded with the substitution amount increasing. Based on these results, small amount of Mn^{4+} and W^{6+} substitution was successfully applied to a base ceramic with the electrical properties satisfied the NP0 specification to miniaturize the grains and enhance the sintering behavior.

Keywords: A. Powder: solid state reaction; C. Dielectric properties; Low sintering; Pyrochlore

1. Introduction

Low-fire bismuth-based ceramics is a typical high frequency dielectrics with high permittivity and low dielectric loss and received special attention with the advances in microelectronic technologies and microwave communication. Bi_2O_3–ZnO–Nb_2O_5 (BZN)-based ceramics with the incorporation of Bi_2O_3–NiO–Nb_2O_5 (BNN) were firstly explored in 1970's as the dielectrics for temperature-stable and temperature-compensating multilayer ceramic capacitors in China [1]. The sintering temperatures of BZN–BNN-based ceramics were found to be below 1000 °C so that high-Ag electrode materials can be used. Similar studies of BZN-based dielectrics were then made by Yan and co-workers [2]. Our previous work indicated that the main phases of BZN-based ceramics are a cubic pyrochlore $Bi_{1.5}ZnNb_{1.5}O_7$ (α phase), dielectric constant ∼170, temperature coefficient of dielectric constant (α_ε) ~ -500 ppm/°C, and a monoclinic pyrochlore $Bi_2Zn_{2/3}Nb_{4/3}O_7$ (β phase), a monoclinic zirconolite-like pyrochlore phase, dielectric constant ∼80, temperature coefficient of dielectric constant (α_ε) $\sim +200$ ppm/°C [3]. Therefore, a two phase composite with NP0 ($\alpha_\varepsilon \leq \pm 30$ ppm/°C between −55 and 125 °C) characteristics is attainable within this system by adjusting the composition with a self-formed α–β co-existing phase structure. The relations of phase equilibrium, crystal structure and dielectric properties were also studied [4]. A high performance BZN-based dielectric with the low sintering temperature below 940 °C satisfied the EIA specification COG was developed for multilayer capacitors, microwave resonators and filters [5]. Because of the strong potentiality in commercial applications of BZN-based dielectrics for microwave multilayer devices, the studies on the microwave properties of BZN materials become more and more active now [6–8]. For improving the properties of the BZN ceramics, some works were performed for studying the influence of the ion substitution and doping in this system [9–11]. The dielectric properties of BZN ceramics are in highly dependent on the additives and compositions.

During the developing the NP0 compositions in BZN system for commercial use, there are two main problems

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* Corresponding author. Fax: +86-29-2668794.
E-mail address: hwang@mail.xjtu.edu.cn (H. Wang).

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continuously inhibit the commercial applications. One is that the dielectric properties, especially the temperature coefficient of the capacitance is highly sensitive to the sintering temperature, another is the abnormal grain growth or secondary recrystallization easily happened [1].

In this paper, the effect of introducing the Mn^{4+} and W^{6+} to substitute the Nb^{5+} in B site which are shared by two ions of different valency [4] of a BZN-based α–β pyrochlore ceramic was investigated. The results show it is an effective way to improve the sinterability and depress the grain growth properties of the ceramics for practical use. The optimized composition with NP0 characteristics is a good candidate for MLCC, LTCC and multiplayer devices in high frequency to microwave ceramics.

2. Experimental

The compositions of BZN-based composition $Bi_{3x}Zn_{2-3x}(Zn_xNb_{2-x-2y}Mn_yW_y)O_7$ ($x = 0.5$–0.65, $y = 0, 0.02, 0.05, 0.1$) with the Mn^{4+} and W^{6+} substituting Nb^{5+} in B site were synthesized by conventional ceramic technology. High purity Bi_2O_3, ZnO, MnO_2, WO_3 and reagent grade Nb_2O_5 were used as starting materials. The constituent oxides were weighed out in proper ratio and mixed with alcohol using agate milling media. The slurries were filtered and dried under an infrared lamp. The dried powders were calcined in air from 750 to 850 °C for 2 h. Then the powders were pressed into discs of 10mm in diameter. The discs were finally sintered from 900 to 1000 °C for 2 h.

The phase structures of BZN samples were characterized by X-ray diffractormetry (XRD). The X-ray diffraction patterns were obtained using a Rigaku D/MAX-2400 X-ray diffractometer with Cu Kα radiation by 0.02° with 2θ steps width. The microstructure characterization was made by a scanning electron microscope (SEM).

Samples for dielectric measurements were painted electrodes with low-temperature-fired silver paste. The dielectric permittivity and dissipation factor of samples were measured using a high precision LCR meter (HP 4284 A). The frequency dependence of the dielectric behavior were measured by a HP 4284 A LCR meter (1 kHz–1 MHz). The electrical resistivity were measured by a HP 4339A high-resistance meter under a measuring voltage of 100 V dc for 1 min. The temperature dependence of the dielectric constant and loss were measured at different frequencies (1, 10 and 100 kHz) and temperature varying from room temperature to 400 °C by placing the discs in an automated measurement system consisting of a PC computer, a HP 4284 A LCR meter and a temperature chamber.

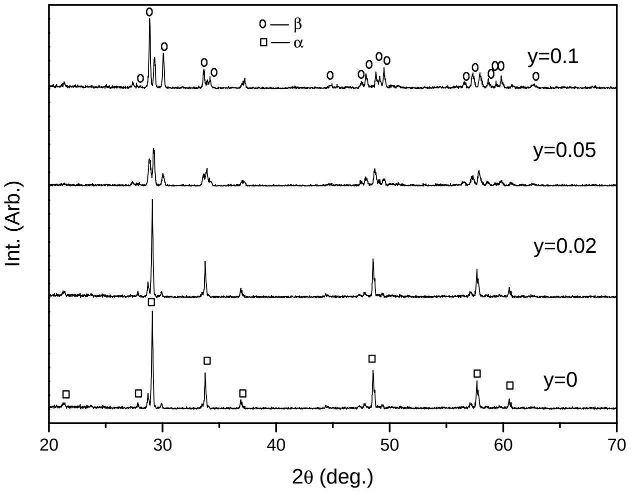


Fig. 1. XRD patterns of $Bi_{3x}Zn_{2-3x}(Zn_xNb_{2-x-2y}Mn_yW_y)O_7$ ($x = 0.5$–0.65, $y = 0, 0.02, 0.05, 0.1$) ceramics sintered at 960 °C for 2 h.

3. Results and discussion

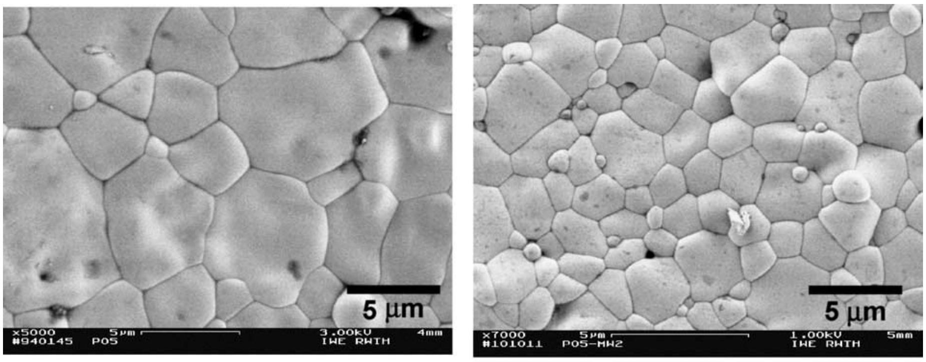
The XRD patterns of the $Bi_{3x}Zn_{2-3x}(Zn_xNb_{2-x-2y}Mn_yW_y)O_7$ ($x = 0.5$–0.65, $y = 0, 0.02, 0.05, 0.1$) ceramics sintered at 960 °C for 2 h were shown in Fig. 1. The crystal structures of the sintered samples were characterized as cubic pyrochlore (α) and monoclinic pyrochlore (β) co-existing phases (α–β). Table 1 presents the phase ratio α of different compositions. The phase ratio of α (in Table 1) was calculated by the following equation:

$$\alpha\,(\%) = \frac{I_\alpha}{I_\alpha + I_\beta} \times 100\% \qquad (1)$$

where I_α, I_β are the intensities of the strongest peak of phases α and β, respectively. The phase ratio α gradually decreases with y value increasing. This indicates that the phase structure gradually changes from the α dominating to β dominating when the amount of substitution increasing. There is no other impurity phase observed in all the patterns. This means that a limited substitutional solid solution with Mn^{4+} and W^{6+} co-substituted Nb^{5+} in B site are formed which

Table 1
The phase ratio, densities and dielectric properties of $Bi_{3x}Zn_{2-3x}(Zn_xNb_{2-x-2y}Mn_yW_y)O_7$ ($x = 0.5$–0.65, $y = 0, 0.02, 0.05, 0.1$) ceramics sintered at 980 °C for 2 h

Composition (y)	α (%)	ε (20 °C, 1 MHz)	$\tan\delta$ (20 °C, 1 MHz)	ρ (Ω cm)	α_ε (85 °C, ppm/°C)	Density (g/cm^3)
0	87	109	0.0001	4.360×10^{13}	−120	7.339
0.02	80	101	0.0001	1.194×10^{14}	−40	7.351
0.05	58	98	0.0003	4.810×10^{12}	+26	7.501
0.1	31	92	0.0004	6.242×10^{11}	+158	7.263



(a) (b)

Fig. 2. SEM photos of $Bi_{3x}Zn_{2-3x}(Zn_xNb_{2-x-2y}Mn_yW_y)O_7$ ($x = 0.5$–0.65) ceramics before and after substitution sintered at 1000 °C for 2 h: (a) $y = 0$ and (b) $y = 0.05$.

attributes to the closed radius of Mn^{4+} (0.054 nm) and W^{6+} (0.066 nm) to that of Nb^{5+} (0.064 nm) and the balanced valence.

The microstructures of the samples were studied by SEM technology. The dense ceramics of the substituted can be obtained after sintered at 960 °C for 2 h. The base ceramic ($y = 0$) has a dense crystal microstructure with bigger grains from 5 to 10 µm at 1000 °C (Fig. 2) and the trace of secondary crystallization can be seen. With the substitution of Mn^{4+} and W^{6+} to Nb^{5+}, the extent of grain abnormally growing up was effectively controlled. For example, the grain size of $y = 0.05$ composition is about 2–3 µm at 1000 °C (Fig. 2). That indicates Mn^{4+} and W^{4+} substitution are effective for depressing the grain growing.

The dielectric properties of the ceramics are listed in Table 1. The base ceramics have excellent electrical resistivity greater than 10^{13} Ω cm. The resistivity reach the summit of 10^{14} Ω cm at $y = 0.02$ but then decreases until 10^{11} Ω cm when $y = 0.1$. With the value of y increasing, the dielectric constant of the samples gradually decreases and the temperature coefficient α_ε increases. The decrease of the dielectric constant is due to the smaller polarizabilities of the Mn (9.4, 10^{-24} cm^3) and W (11.1, 10^{-24} cm^3) than that of Nb (15.7, 10^{-24} cm^3). The dielectric dissipation factor of the samples at room temperature is on the order of 10^{-4} at 1 MHz before and after substitution. The frequency dependency of dielectric behaviors of the ceramics is shown in Fig. 3. The dielectric constants of the different compositions vary slightly with the frequency varying. The dielectric loss diminishes with the frequency increasing which is due to the leakage conduction. The higher the substitution amount, the larger the decrease of dielectric loss is. The temperature dependence of dielectric behaviors of the ceramics is shown in Fig. 4. The temperature coefficient α_ϵ was calculated by the following formula:

$$\alpha_\varepsilon = \frac{\varepsilon_{T_2} - \varepsilon_{T_1}}{\varepsilon_{T_1}(T_2 - T_1)} \tag{2}$$

where ε_{T_1} is the dielectric constant at T_1 (here, T_1 is 25 °C), and ε_{T_2} is the dielectric constant at T_2 (here, T_2 is 85 or 125 °C). The temperature dependence of the dielectric behavior shows that both ϵ and tanδ goes up with the temperature rising at lower frequencies. The higher the substitution amount, the lower the onset point. This indicated

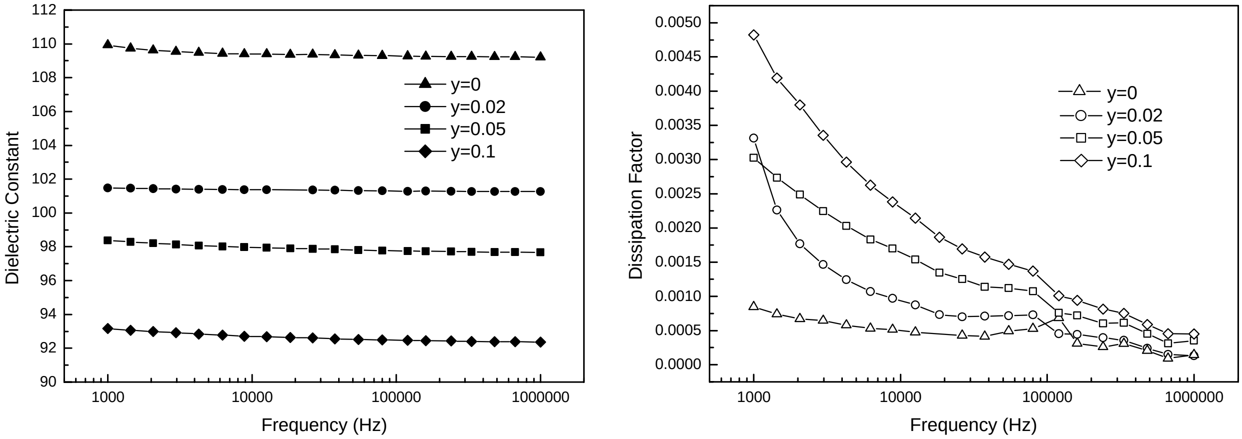


Fig. 3. Frequency dependence of $Bi_{3x}Zn_{2-3x}(Zn_xNb_{2-x-2y}Mn_yW_y)O_7$ ($x = 0.5$–0.65, $y = 0$, 0.02, 0.05, 0.1) ceramics sintered at 960 °C for 2 h.

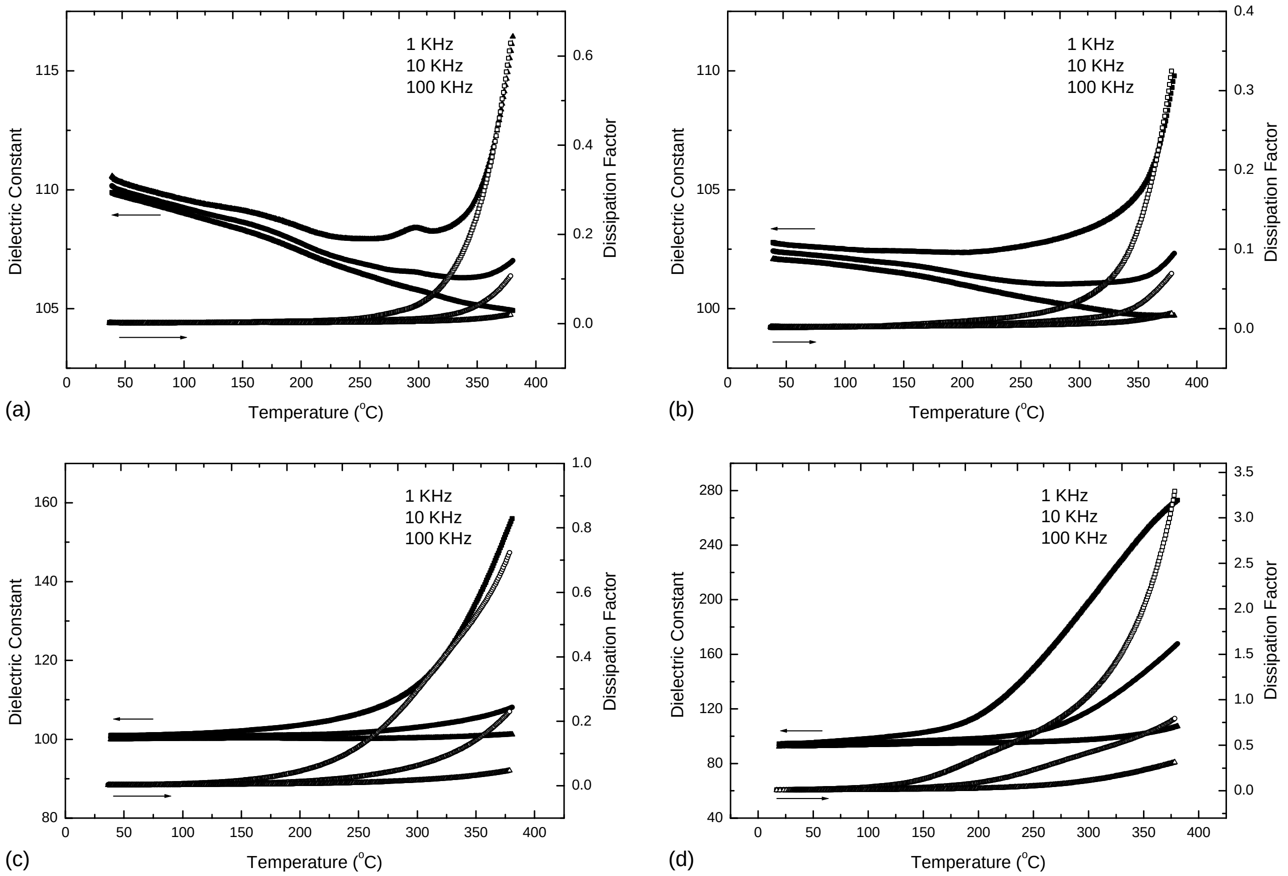


Fig. 4. Temperature dependence of $Bi_{3x}Zn_{2-3x}(Zn_xNb_{2-x-2y}Mn_yW_y)O_7$ ($x = 0.5$–0.65, $y = 0$ (a); 0.02 (b); 0.05 (c); and 0.1 (d)) ceramics sintered at 960 °C for 2 h.

that the typical leakage conductance of high temperature existed. With the temperature increasing, electrical conductivity increases due to the increase in thermally activated drift mobility of electric charge carriers according to the hopping conduction mechanism [12]. This is in accordance with the results of frequency dependency. Since the radius of Mn^{4+} is smaller than that of Nb^{5+}, the mobility of electric charge carriers in B site increases with the amount of substitution increasing.

Since the MnO_2 and WO_3 in the ratio of 1:1 are introduced for substitution of Nb_2O_5, The substitution will lead a dynamic equivalence in ideal state as in the following:

$$2MnO_2 \xrightarrow{Nb_2O_5} 2Mn'_{Nb} + 4O_O^{\times} + V_O^{\bullet\bullet} \tag{3}$$

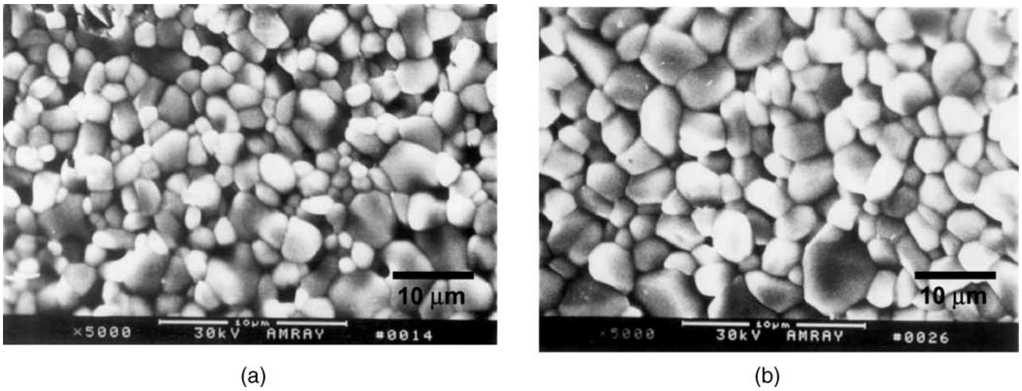
$$2WO_3 \xrightarrow{Nb_2O_5} 2W_{Nb}^{\bullet} + 5O_O^{\times} + \tfrac{1}{2}O_2 + e' \tag{4}$$

However, if the MnO_2 introduced with some reductive MnO then more oxygen vacancies will be produced in such a situation:

$$2MnO \xrightarrow{Nb_2O_5} 2Mn'''_{Nb} + 2O_O^{\times} + 3V_O^{\bullet\bullet} \tag{5}$$

Combined with the measurement results of the electrical properties, it could be deduced that some lattice defects such as oxygen vacancies occurred when the substitution amount increasing. This situation is easy to happen when the Mn^{4+} change its valence of +4 to lower valence of +2. Noticed that densities of the samples first increase with the substitution amount increasing to $y = 0.05$ then anomaly decrease to the lowest when the substitution amount continuously increasing to $y = 0.1$ (Table 1). Considering the mean atomic weight of Mn and W (119.389) in 1:1 is bigger than that of Nb (92.906), the density should increase continuously with the substitution amount increasing. The decreased density of $y = 0.1$ results more porosities in the sample. Both the porosity and the lattice defects would be responsible for the degrading of the dielectric behavior of $y = 0.1$.

For improving the dielectric properties and inhibiting the grain growing up in the NP0 composition in BZN system for practical use, the small amount of Mn^{4+} and W^{6+} substitution in B site for the Nb^{5+} was adopted. Table 2 presents the dielectric properties of the NP0 compositions in BZN system before and after Mn^{4+} and W^{6+} substitution. The α_ε changes only ±16 ppm/°C in the optimized composition comparing with 69 ppm/°C of the base NP0 composition at the sintering temperature range from 940 to 980 °C. Fig. 5 is the SEM photos of the optimized composition sintered at 940–980 °C. It showed that the grain growing was well controlled and there is no abnormal grain growth. The grain



(a) (b)

Fig. 5. SEM micrographs of Mn^{4+} and W^{6+} substituted BZN-based NP0 ceramics (after substitution) sintered at 940 °C for 2 h (a) and 980 °C for 2 h (b).

Table 2
Dielectric properties of BZN-based NP0 ceramics before and after optimized by Mn^{4+} and W^{6+} substitution

Sintering temperature/ soaking time	NP0 (before substitution)			NP0 (after substitution)		
	ε	$\tan\delta$	α_c	ε	$\tan\delta$	α_c
920 °C/2 h	77	6	+139	90	7	+91
940 °C/2 h	95	9	+53	99	3	+16
960 °C/2 h	98	8	+26	99	3	−9
980 °C/2 h	101	7	−16	100	3	−16
1000 °C/2 h	101	7	−64	100	3	−25

ε, $\tan\delta(10^{-4})$: at 1 MHz; α_c (ppm/°C): at 100 kHz, 85 °C.

size of 940 °C is 1–2 μm and that of 980 °C is 2–3 μm. The improving characteristics attribute to the relatively stable phases constitution and fine grains. This composition seems to be a good candidate for the practical use of multiplayer devices in high frequency and microwave field.

4. Conclusion

The ion substitution with Mn^{4+} and W^{6+} co-substituted Nb^{5+} in B site of a cubic-monoclinic co-exsisting pyrochlore ceramic $Bi_{3x}Zn_{2-3x}(Zn_xNb_{2-x-2y}Mn_yW_y)O_7$ ($x = 0.5$–0.65, $y = 0$, 0.02, 0.05, 0.1) was investigated. The experimental results show that dielectric constant (ε) decreases while the temperature coefficient of dielectric constant (α_ε) increases with the increasing of the y value. The Mn^{4+} and W^{6+} substituted Nb^{5+} in B site effectively depressed the grain growth and the fine grain ceramics (1–3 μm) were obtained. The electrical resistivity was also enhanced in smaller substitution amount at $y = 0.02$ but degraded with the substitution amount increasing to $y = 0.1$. This probably attributes to the porosities and multi-valences of manganese that leads to the lattice defects. Small amount of Mn^{4+} and W^{6+} co-substitution in the NP0 compositions in BZN system stabilize the phase constitution and dielectric temperature coefficients of the samples.

Acknowledgements

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