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Optimization of dielectric constant temperature coefficient of pyrochlores containing bismuth①

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Abstract: The Bi_2O_3-ZnO-Nb_2O_5(BZN)-based ceramic samples were prepared according to the optimum composition of $(Bi_{3x}Zn_{2-3x})(Zn_xNb_{2-x})O_7$ by solid state reaction. The BZN ceramic structure and the dielectric properties were explored via X-ray diffractometer(XRD), differential thermal analysis(DTA), scanning electron microscope (SEM), and HP4275A impedance analysis. The amphoteric surface active agent with alcohol amine double nature is introduced when the raw materials are mixed and ground. The anatase titania doped BZN-based ceramics was also investigated. Either doping the anatase TiO_2 or adding the surface active agent or both of them can widen sintering temperature range which satisfies the zero temperature coefficient ($0 \pm 30 \times 10^{-6}$/ ℃) of the BZN ceramics. And these BZN ceramics with diphasic pyrochlore structure possess excellent dielectric properties.

Key words: Bi_2O_3-ZnO-Nb_2O_5 ceramic; phase transformation; dielectric properties
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1 INTRODUCTION

Dielectric ceramics are widely used with advances in microelectronic technologies. Bismuth-based pyrochlores exhibit well-known high-frequency dielectric properties for multilayer capacitor. Group of pyrochlore structured compounds is of general formula $A_2B_2O_7$(where A is trivalent or bivalent cations and B is quadrivalent and quinquevalent cations). As a member of the pyrochlore family of compound, bismuth zinc niobate is a typical high frequency dielectrics with high permittivity and low dielectric loss, and can be applied as various devices, such as temperature-stable multilayer ceramics capacitor(MLC) and microwave resonator and filter. Bismuth zinc niobate system was reported for the first time by the Chinese engineers in 1970s while wide recognition in world began in 1990s[1-3]. Recently, this system attracts more and more attentions[4-14]. Much work has been performed on the crystal structures and improving dielectric properties, especially enhancing permittivity and reducing dielectric loss. However, the optimization of dielectric constant temperature coefficient of pyrochlores containing bismuth has not been reported. Moreover, because the temperature coefficient of BZN-based ceramics is very sensitive to the change of the sintering temperature, it cannot be used in MLC industry on a large scale[15, 16]. Besides, with the developing trend to get smaller and thinner multilayer devices, one of the major bottlenecks for the practical applications in this low-firing system is how to control the grain growth to gain the fine grain ceramics.

The present paper reports the optimization of dielectric constant temperature coefficient of pyrochlores containing bismuth with composition corresponding to $(Bi_{3x}Zn_{2-3x})(Zn_xNb_{2-x})O_7$ system. The effects of adding the surface active agent and the effects of anatase TiO_2 doping on the phase composition, grain size and dielectric properties of BZN-based ceramics are investigated.

2 EXPERIMENTAL

Reagent Bi_2O_3, ZnO, and Nb_2O_5 were weighed in a proper mole ratio according to the compositions $(Bi_{3x}Zn_{2-3x})(Zn_xNb_{2-x})O_7$ ($0.15 < x < 0.85$) and mixed in alcohol with agate media for 4 h. The slurry was dried and then calcined at 770 ℃ for 2 h and milled again for 4 h. The dried powers were then granulated and pressed into pellets. Samples were sintered at 940 - 1 040 ℃ for 2 h. Four kinds of experimental designs were planned: 1) the original BZN samples; 2) BZN samples with adding the surface active agent (abbreviated as SAA); 3) anatase TiO_2-doped BZN samples; 4) SAA-added and anatase TiO_2-doped BZN samples. It was in the first mixing process of the oxides that the SAA was added. And the SAA is the ampho-

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teric surface active agent with alcohol amine double nature, whose equilibrium value (hydrophilic lipophilic balance (HLB)) is 9.4. Besides, the amount of the SAA added was 1% (mass fraction). And the amount of the anatase TiO_2 added was 8.6% (molar fraction).

X-ray diffraction (XRD) patterns were obtained with a Rigaku D/MAX-2400 X-ray diffractometer with Cu K_α radiation. Differential thermal analysis (DTA) curves were obtained with Thermal Analyzer 2000. And the microstructures of the samples were observed by the JXA-840 scanning electron microscope (SEM). The particle size data of the powder were obtained with Coulter Particle Analyzer. The temperature dependence of the dielectric constant was measured in an automated measurement system consisting of a PC computer, an HP 4275A LCR meter, an HP 6942A multiprogrammer, and a temperature chamber. The temperature range were between − 70 ℃ and 130 ℃. The measuring frequency was 1 MHz. An HP-4140B PA meter was used to measure the resistivity of the samples (about 1 mm thick) under 100 V dc voltage for 1 min.

3 RESULTS

3.1 Phase composition

Fig. 1 and Fig. 2 show the XRD patterns of the BZN samples calcined at 770 ℃ for 2 h and sintered from 940 ℃ to 1 040 ℃ for 2 h, respectively. The percentage of cubic pyrochlore phase (PDF 25-443, abbreviated as α phase) or orthorhombic pyrochlore phase (PDF 330-711, abbreviated as β phase) is calculated according to the following equation:

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

where I_α and I_β are the strongest diffraction intensities of the α phase and β phase, respectively (Table 1).

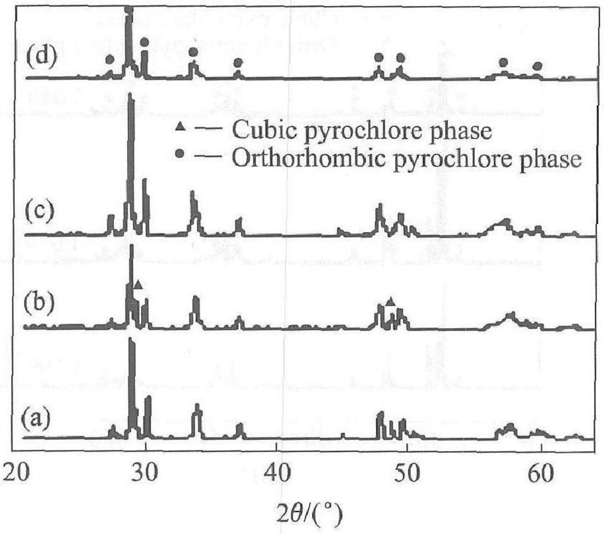

Fig. 1 XRD patterns of BZN

From the XRD analysis, all the BZN samples are found to have α-β coexisting phase structure. The sintering temperature is dropped by doping the anatase TiO_2. And the phase transformation from β phase to α phase is performed with increasing sintering temperature. Either doping the anatase TiO_2 or adding the surface active agent or both of them can restrain the phase transition from β phase to α phase.

3.2 Scanning electron micrograph

Fig. 3 presents the SEM images of the sintered BZN-based ceramics. Compared with the original BZN ceramic sintered at 1 000 ℃ for 2 h, the surface active agent added and anatase TiO_2-doped BZN ceramic is of smaller and more homogeneous grains.

3.3 Dielectric properties

The dielectric properties of the sintered BZN-based ceramics are listed in Table 2. The temperature coefficient α_ε is calculated by the following equation:

Table 1 Phase composition of calcined BZN samples and sintered BZN samples

BZN Samples	Phase composition of calcined BZN samples		Phase composition of sintered BZN samples		
	w(α phase)/%	w(β phase)/%	Sintering temperature/℃	w(β phase)/%	w(α phase)/%
Original	23.3	76.7	1 000 1 040	70.0 46.8	30.0 53.2
SAA-added	26.2	73.8	1 000 1 040	72.2 56.2	27.8 43.8
TiO_2-doped	13.8	86.2	960 1 000	74.0 60.6	26.0 39.4
SAA-added and TiO_2-doped	19.2	80.8	940 980	64.3 52.9	35.7 47.1

α phase —Cubic pyrochlore phase; β phase —Orthorhombic pyrochlore phase

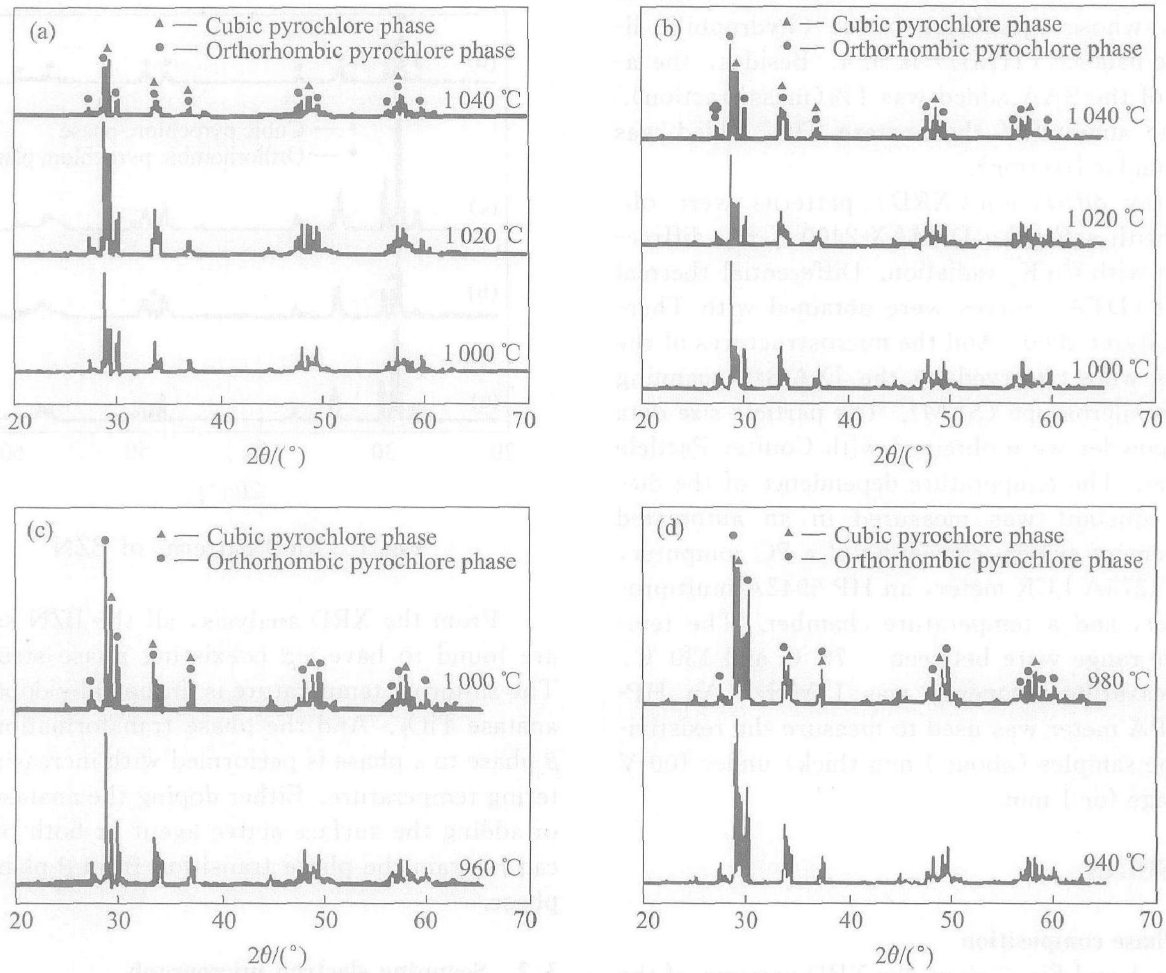

Fig. 2 XRD patterns of sintered BZN ceramic samples
(a) —Original; (b) —SAA-added; (c) —Anatase TiO_2-doped; (d) —SAA-added and TiO_2-doped

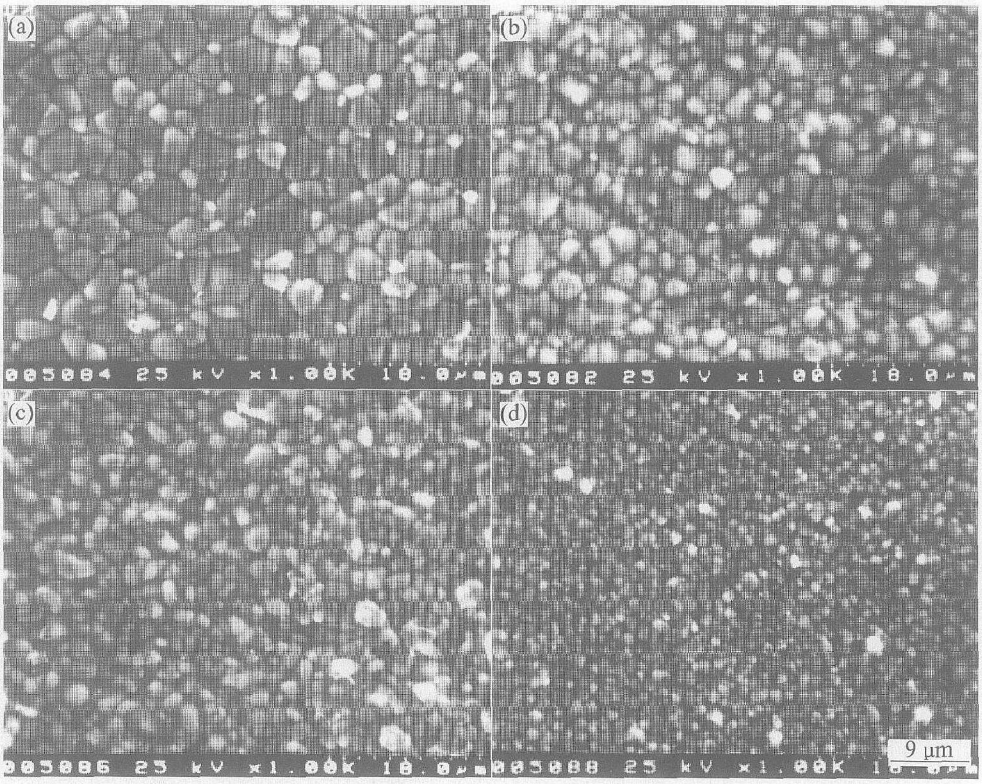

Fig. 3 SEM micrographs of BZN-based ceramic samples sintered at 1 000 ℃ for 2 h
(a) —Original; (b) —TiO_2-doped; (c) —SAA-added; (d) —SAA-added and TiO_2-doped

Table 2 Dielectric properties of BZN ceramic samples

BZN Samples	Sintering temperature/ ℃	$\alpha_c / 10^{-6}$ ℃$^{-1}$			ρ (Ω • cm)	tan δ (1 MHz)	ε (20 ℃, 1 MHz)
		− 55 ℃	85 ℃	125 ℃			
Original	1 000	28	12	5	$> 10^{13}$	< 0.000 1	96.2
	1 020	− 7	− 18	− 23	$> 10^{13}$	< 0.000 1	107.0
	1 040	− 45	− 85	− 90	$> 10^{13}$	< 0.000 1	120.9
SAA-added	1 000	20	9	3	$> 10^{13}$	< 0.000 1	98.9
	1 020	17	4	1	$> 10^{13}$	< 0.000 1	97.3
	1 040	− 12	− 19	− 23	$> 10^{13}$	< 0.000 1	99.7
TiO_2-doped	960	18	21.7	23.5	$> 10^{13}$	< 0.000 1	91.5
	1 000	− 15	− 24	− 24	$> 10^{13}$	< 0.000 1	98.9
SAA-added and TiO_2-doped	940	1	− 1	− 2.9	$> 10^{13}$	< 0.000 1	97.3
	980	− 27	− 30	− 29	$> 10^{13}$	< 0.000 1	100.6

$$\alpha_c = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 \times (t_2 - t_1)} \qquad (2)$$

where ε_1 is the dielectric constant at t_1 (here t_1 is 20 ℃), and ε_2 is the dielectric constant at t_2 (here t_2 is − 55 ℃, 85 ℃, and 125 ℃, respectively).

Depending on the zero temperature coefficient $(0 \pm 30 \times 10^{-6}/$ ℃), the sintering temperature of the BZN ceramics is in the range of 1 000 − 1 020 ℃ for the original samples, 1 000 − 1 040 ℃ for the surface active agent added samples, 960 − 1 000 ℃ for the TiO_2-doped samples, and 940 − 980 ℃ for surface active agent added and TiO_2-doped samples, respectively.

4 DISCUSSION

In BZN-based diphasic ceramics, the formation of β phase structure may be related to the coupling of $6s^2$ lone pair electrons of Bi^{3+} ions[16]. If the sites of the pyrochlore structure are occupied by Bi^{3+} ions only, the coupling among $6s^2$ lone pairs might cause distortion of the cell and only β phase occurs. When a certain number of Zn^{2+} ions enter the A sites with increasing sintering temperature ($t > 700$ ℃), the coupling of $6s^2$ lone pair electrons among Bi^{3+} ions is broken, and α phase appears.

The physical properties of the powders Bi_2O_3, ZnO, and Nb_2O_5 are different ($\rho_{Bi_2O_3} > \rho_{ZnO} > \rho_{Nb_2O_5}$, where ρ represents the density; $d_{Bi_2O_3} > d_{ZnO} > d_{Nb_2O_5}$, where d represents the particle size), so the segregation phenomenon appears much easily during the raw material mixing process. In the BZN-based diphasic ceramics with the surface active agent added, the surface active agent wets the powder and forms the adsorbed layer on the surface of the solid particles, which weakens the surface tension of the interface between solid and liquid and enhances the dispersivity of the powders in the liquid media when they are milled. This is beneficial to overcoming the shortcoming of insufficient mixing in conventional ceramic processing. Therefore, Bi_2O_3, ZnO and Nb_2O_5 are mixed sufficiently. Moreover, during the following sintering process, the energy consumption is necessary for a certain number of Zn^{2+} ions entering from B sites to A sites. Because there are more carbohydrate polymers (5% PVA and 1% SAA) which decompose at lower temperature in sintering, the looseness and porosity of the BZN samples are increased. The energy produced by the temperature increasing from 950 ℃ to 1 050 ℃ is also exhausted by the denseness of the BZN samples. So, there is an approximate terrace at which heat is neither absorbed nor released from 950 ℃ to 1 050 ℃ in the DTA curve (Fig. 4). And there is less transformation from β phase to α phase.

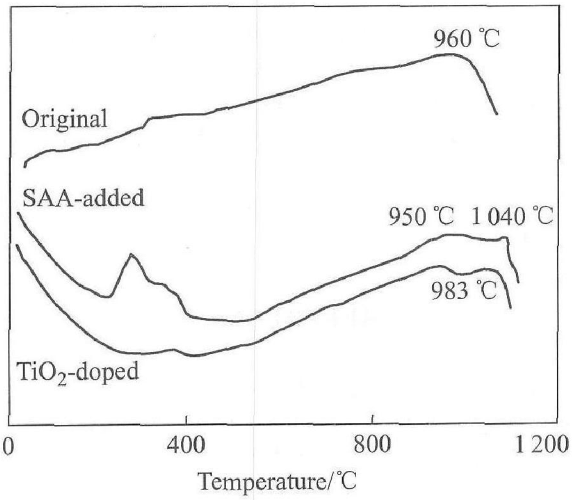

Fig. 4 DTA curves of BZN

In anatase TiO_2-doped BZN-based diphasic ceramics, the Ti^{4+} ($d = 0.068$ nm) is supposed to enter the B sites whose ion radius requirement is about 0.06 − 0.07 nm[17]. So, its composition can be expressed as $(Bi_{3x}Zn_{2-3x})(Zn_xNb_{2-x-y}Ti_y)O_7$. And the stability of BZN-based pyrochlore structure is enhanced because of the more reasonable matching in both ion radius and electronic valence after the anatase TiO_2 is doped. In addition, there is a phase transformation from anatase TiO_2 to rutile TiO_2, whose endothermic value is about 1.256 kJ/mol[18]. Thus, there is an approximate terrace at which heat is neither absorbed nor released in the temperature range of 983 ±60 ℃ in the DTA curve (Fig. 4). During the following sintering process, the process that a certain number of Zn^{2+} ions in B sites enter the A sites needs energy consumption; at the same time, the TiO_2 phase transformation also exhausts the energy. So, there is less transformation from β phase to α phase.

In the sintering process of the anatase TiO_2-doped BZN-based diphasic ceramics with surface active agent added, there are mainly four changes needed to absorb the energy: 1) the grains of the α phase and β phase grow; 2) a certain number of Zn^{2+} ions in B sites enter the A sites so as to complete the phase transformation from β phase to α phase; 3) the denseness of the samples is expected because of the looseness caused by the more amount of the carbohydrate polymers added; 4) the anatase TiO_2 transforms to rutile TiO_2. Accordingly, the grain growth of the BZN-based diphasic ceramics is controlled (Fig. 3(d)), and the phase transformation from β phase to α phase is also restrained.

The temperature coefficient of the BZN ceramics with pure α phase structure is negative (-4×10^{-4}/℃) and that of the BZN ceramics with pure β phase is positive (1.5×10^{-4}/℃)[19]. The temperature coefficient of BZN ceramics with α-β coexisting phases depends on the content ratio of α phase to β phase. The zero temperature coefficient of BZN ceramics can be obtained in a proper content ratio of α phase to β phase. So, the smaller the change of the content ratio of β phase to α phase, the smaller the change of the temperature coefficient with increasing sintering temperature (Table 1 and Table 2).

REFERENCES

[1] WANG Zhen-ping, ZHANG Shi-ying. No lead low-fired multilayer ceramic capacitor (MLC) dielectric materials [J]. Electron Compon Mater, 1985, 4(8): 383 - 389. (in Chinese).

[2] Yan M F, Ling H C, Rhodes W W. Low-firing temperature stable dielectric compositions based on bismuth nickel zinc niobates [J]. J Am Ceram Soc, 1990, 73(4): 1106 - 1109.

[3] Ling H C, Yan M F, Rhodes W W. High dielectric constant and small temperature coefficient bismuth-based dielectric composition [J]. J Mater Res, 1990, 5 (8): 1752 - 1762.

[4] WANG Hong, DU Hui-ling, YAO Xi. Structural study of Bi_2O_3-ZnO-Nb_2O_5 based pyrochlores [J]. Materials Science and Engineering, 2003, B99: 20 - 24.

[5] Valant M, Suvorov D. Dielectric properties of the fluorite-like Bi_2O_3-Nb_2O_5 solid solution and the tetragonal Bi_3NbO_7[J]. J Am Ceram Soc, 2003, 86(6): 939 - 944.

[6] WANG Hong, Elsebrock R, Schneller T, et al. Bismuth Zinc niobate ($Bi_{1.5}ZnNb_{1.5}O_7$) ceramics derived from metallo-organic decomposition precursor solution [J]. Solid State Communications, 2004, 132: 481 - 486.

[7] Choi G K, Kim D W, Cho S Y, et al. Influence of V_2O_5 substitutions to ($Bi_2(Zn_{1/3}Nb_{2/3})O_7$ pyrochlore on sintering temperature and dielectric properties [J]. Ceramics International, 2004, 30: 1187 - 1190.

[8] Cheng H F, Chen Y C, Liu H L, et al. Correlation of microwave dielectric properties and crystalline for pulsed laser deposited $Bi_2(Zn_{1/3}Nb_{2/3})O_7$ thin films [J]. J European Ceramic Society, 2004, 24: 1791 - 1794.

[9] Andrew L H, Seth B W. Synthesis and structural study of stoichiometric $Bi_2Ti_2O_7$ pyrochlore [J]. Journal of Solid State Chemistry, 2004, 177: 139 - 145.

[10] YI Hu, Huang C L. Structural characterization of Bi-Zn-Nb-O cubic pyrochlores [J]. Ceramics International, 2004, 30: 2241 - 2246.

[11] WANG Hong, DU Hui-ling, PENG Zhen, et al. Improvements of sintering and dielectric properties on Bi_2O_3-ZnO-Nb_2O_5 pyrochlore ceramics by V_2O_5 substitution [J]. Ceramics International, 2004, 30: 1225 - 1229.

[12] Levin I, Amos T G, Nino J C, et al. Structural study of an unusual cubic pyrochlore $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ [J]. Journal of Solid State Chemistry, 2002, 168: 69 - 75.

[13] Valant M, Davies P K. Crystal chemistry and dielectric properties of chemically substituted ($Bi_{1.5}Zn_{1.0}$-$Nb_{1.5})O_7$ and $Bi_2(Zn_{2/3}Nb_{4/3})O_7$ pyrochlore [J]. J Am Ceram Soc, 2000, 83: 147 - 153.

[14] DU Hui-ling, YAO Xi. Dielectric relaxation characteristics of bismuth zinc niobate pyrochlores containing titanium [J]. Physica B, 2002, 324: 121 - 126.

[15] REN Qing-li. The Properties of Multilayer Ceramic Capacitors of Bi_2O_3-ZnO-Nb_2O_5-based Ceramics and the Optimization of its Ceramics [D]. Xi'an: Xi'an Jiaotong University, 1999. 7 - 43. (in Chinese)

[16] WANG Xiao-li, WANG Hong, YAO Xi. Structure, phase transformations, and dielectric properties of pyrochlores containing bismuth [J]. J Am Ceram Soc, 1997, 80: 2745 - 2748.

[17] Aleshine E, Roy R. Crystal chemistry of pyrochlore [J]. J Am Ceram Soc, 1962, 45(1): 18 - 25.

[18] Academy of Tianjing Chemical Engineering. Handbook of Inorganic Compound Industry [M]. Beijing: Chemical Industry Press, 1992. 168 - 169. (in Chinese)

[19] HUANG Biao. Study for the Structure and Properties of BZN System Ceramics and BPN System Ceramics Containing Bismuth [D]. Xi'an: Xi'an Jiaotong University, 1993. 15 - 30. (in Chinese)

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