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Improvements of sintering and dielectric properties on Bi_2O_3–ZnO–Nb_2O_5 pyrochlore ceramics by V_2O_5 substitution

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Abstract

The effects of V_2O_5 on the phase formation and dielectric properties of Bi_2O_3–ZnO–Nb_2O_5 (BZN) pyrochlore ceramics were investigated. With the small amount of V_2O_5 substitution ($0.005 \leq x \leq 0.05$), the sintering temperatures of $Bi_{1.5}Zn_{0.5}(Zn_{0.5}Nb_{1.5-x}V_x)O_7$ can be effectively reduced from 1000 to 840 °C while the phase structures still kept to be the pure cubic pyrochlores. The V_2O_5 seems to provide an eutectic melt below the sintering temperature to improve the sinterability. The dielectric constants decrease gradually with V_2O_5 substitution while the temperature coefficients of the samples continuously increase. The dielectric loss are in same level as that of the basic composition at the smaller substitute amount ($x \leq 0.02$) but then degraded in lower frequency when the substitution reached to $x = 0.05$. Obvious dispersion in the dielectric constant and loss was observed as a function of frequency and temperature after the substitution.

Keywords: A. Powders: solid state reaction; C. Dielectric properties; Pyrochlore

1. Introduction

Bi_2O_3–ZnO–Nb_2O_5 (BZN) based pyrochlore ceramics were first explored in 1970s by Chinese engineers for low firing temperature multilayer capacitors [1]. Recently, this system attracts more and more attentions due to its excellent dielectric properties in rf and microwave range. Previous work revealed that there are two main phases in the system: a cubic pyrochlore phase $Bi_{1.5}ZnNb_{1.5}O_7$, dielectric constant ~170, temperature coefficient of capacitance (TCC) ~−500 ppm/°C, and a monoclinic zirconolite-like pyrochlore phase $Bi_2Zn_{2/3}Nb_{4/3}O_7$, dielectric constant ~80, temperature coefficient of capacitance (TCC) ~+200 ppm/°C [2,3]. Its high dielectric constants, relatively low dielectric losses (high quality value), controllable TCC with the low sintering temperatures (below 1000 °C) make this system a very appealing candidate for the application to low-fire high-frequency multiplayer devices. The relations of phase equilibrium, crystal structure and dielectric properties in this system were studied and a high performance BZN-based NPO dielectric with the low-firing temperature below 940 °C was developed for multilayer capacitors, microwave resonators and filters [4–6]. Recent publications have reported the formation, stability, dielectric relaxation and crystallographic characterization in this system as well as successful manufacturing of prototype devices include LC filters and low temperature co-firing ceramic (LTCC) systems [7–11]. Previous works found that the doping of CuO and V_2O_5 in $BiNbO_4$ ceramics improved the sinterability as well as microwave dielectric properties of $BiNbO_4$ ceramics [12–14]. Doping V_2O_5 on the Bi_2O_3–NiO–Nb_2O_5 (BNN) and Bi_2O_3–ZnO–Nb_2O_5 complex mixtures was also tried [15]. Anyway, the mixed compositions and process technology in that work are quite complicated.

According the principles of crystal chemistry, the V^{5+} is suitable for being introduced in the B site to substitute Nb^{5+} in BZN pyrochlores due to its closed ionic radius, polarizability and same valence. Moreover, the melt point of V_2O_5 is 690 °C and it can react with the ZnO eutectically [15], therefore it can be a good candidate for using as sintering aids to reduce the sintering temperature needed for densifying the dielectrics.

In this paper, we introduce the vanadium pentoxide to the $Bi_{1.5}ZnNb_{1.5}O_7$ cubic pyrochlore ceramic to form substitutional solid solutions by solid reaction process. It

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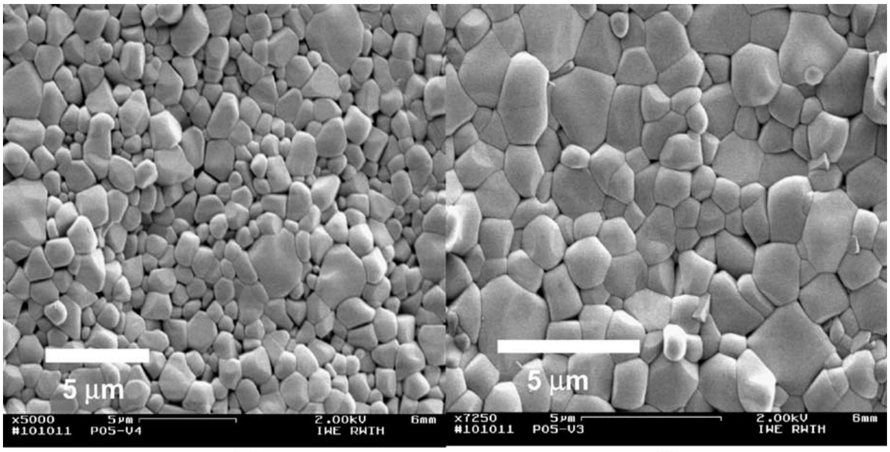

(a) (b)

Fig. 1. SEM pictures of $Bi_{1.5}Zn_{0.5}(Zn_{0.5}Nb_{1.5-x}V_x)O_7$ ceramics sintered at 840°C for 2 h: (a) $x = 0.02$ and (b) $x = 0.05$.

should be pointed out that here the ion substitution rather than ion doping is used to maintain the structure as it is before substitution and avoid the second phase forming. The effect of the V^{5+} substitution on the sintering temperature, phase structure and dielectric properties of $Bi_{1.5}Zn_{0.5}(Zn_{0.5}Nb_{1.5-x}V_x)O_7$ dielectric properties were then reported.

2. Experimental

The compositions of $Bi_{1.5}Zn_{0.5}(Zn_{0.5}Nb_{1.5-x}V_x)O_7$ ($x =$ 0, 0.005, 0.01, 0.02, 0.05) were synthesized by conventional powder processing technology. High purity Bi_2O_3, ZnO, V_2O_5 and reagent grade Nb_2O_5 were used. 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. Dried powders were pressed into disks of 10 mm in diameter. The samples were calcined in a covered corundum crucible in air at 840–1000 °C for 2 h. The density of the ceramic sample was measured by the Archimedes method. The electrodes were then made using silver paste.

The powder X-ray diffraction (XRD) was made by a Philips X'pert X-ray diffractometer, Cu Kα, 40 kV–45 mA. The scanning step 0.02° with an interval of 2 s and the diffraction lines in the 2θ range of 10–80° were collected and used for the determination of lattice parameters. The morphology of sintered ceramics was studied by scanning electron microscopy (SEM) using a Zeiss Gemini electron microscope.

The electrical resistivity of the sample was measured by a HP 4339 A high resistance meter under a 100 V dc bias for 1 min. A HP4284A LCR meter was used for measuring the frequency dependency of room temperature dielectric behaviors from 1 kHz to 1 MHz. Dielectric measurements as a function of temperature were carried out using a HP4284 A LCR meter in conjunction with a computer controlled temperature chamber at four different frequencies (1, 10, 100 kHz and 1 MHz) and temperatures range of RT to 300 °C.

3. Results and discussion

The calcined powder has good sinterability and the dense ceramics were obtained easily at the temperature from 840 to 940 °C. After the V^{5+} was introduced for the substitution of Nb^{5+} in BZN ceramic, the sintering temperature of the substituted sample was lower down significantly. The sintering temperature of unsubstituted basic composition $Bi_{1.5}Zn_{0.5}(Zn_{0.5}Nb_{1.5})O_7$ is 1000 °C, while that of the $Bi_{1.5}Zn_{0.5}(Zn_{0.5}Nb_{1.5-x}V_x)O_7$ ceramics are 900 °C ($x =$ 0.005), 880 °C ($x = 0.01$), 840 °C ($x = 0.02$) and 840 °C ($x = 0.05$), respectively. All the sintered samples have very

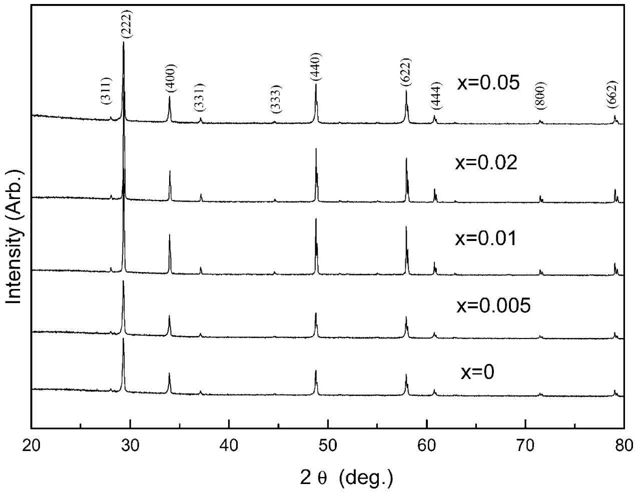

Fig. 2. XRD patterns of $Bi_{1.5}Zn_{0.5}(Zn_{0.5}Nb_{1.5-x}V_x)O_7$ pyrochlore ceramics.

Table 1
The dielectric properties of $Bi_{1.5}Zn_{0.5}(Zn_{0.5}Nb_{1.5-x}V_x)O_7$ ceramics

Composition (x)	ε (20°C, 1 MHz)	tan δ (20 °C, 1 MHz)	ρ (Ω cm)	TCC (ppm/°C), 85 °C	TCC (ppm/°C), 125 °C
0	170	0.0001	$\geq 10^{13}$	−515	−520
0.005	162	0.0004	$\geq 10^{13}$	−431	−448
0.01	157	0.0003	$\geq 10^{13}$	−407	−420
0.02	151	0.0003	$\geq 10^{13}$	−396	−411
0.05	142	0.0011	$\geq 10^{12}$	−349	−348

high relative densities from 99.0 to 97.5% with the amount of V^{5+} substitution increasing. The SEM analysis revealed the dense structure can be obtained (Fig. 1) after the substitution at the sintering temperature as lower as 840 °C. The grain size increases with the amount of V_2O_5 increasing. It seems that V_2O_5 provides an eutectic melt with Bi_2O_3 and ZnO below the sintering temperature to improve the sinterability. The higher the amount of V_2O_5 is, the lower the sintering temperature is.

V^{5+} has smaller ionic radius ($r(V^{5+}) = 0.054$ and $r(Nb^{5+}) = 0.064$ nm) than that of Nb^{5+}. The XRD analysis revealed that the phase structures of substituted sample are still pure pyrochlores (Fig. 2) and no second phase was observed. The lattice parameters of the substituted samples keep stable at the same value of 1.055 nm as that of the basic composition. That means V^{5+} partly substituting for Nb^{5+} at B site results a relatively stable substitutional solid solution $Bi_{1.5}Zn_{0.5}(Zn_{0.5}Nb_{1.5-x}V_x)O_7$ ($x \leq 0.05$) and there is no structure distortion happens. The densities of the samples decreased linearly with the V^{5+} amount increasing and this seems attributes to the relative lower atomic weight of V (50.9415) than that of Nb (92.9064).

Table 1 presents the data collected of the series samples at 1 MHz. As expected, the V^{5+} substitution induces significant changes on the dielectric properties. The dielectric constant decreases gradually from 162 to 147. The decrease of dielectric constant is associated with the smaller polarizability of V than that of Nb (12.4 of V and 15.7 of Nb, 10^{-24} cm^3). The dielectric loss keeps as lower as that of the basic composition (tan $\delta \leq 4 \times 10^{-4}$) and the resistivity is larger than 10^{13} for the compositions $x < 0.02$. The dielectric loss begins to increase when $x \geq 0.05$ and the resistivity decreases to 10^{12} simultaneously. The temperature coefficient continuously increases with the substitution amount increasing from −520 to −348 ppm/°C. It is noticed that the V^{5+} substitution can increase the temperature coefficient with the decrease of dielectric constant while the dielectric loss remains in the same lower level as that before substituted (See that of $x = 0.02$).

Fig. 3 shows the frequency dependency of the dielectric and dielectric loss of the series samples at room temperature. The curves of dielectric constant and dielectric loss remain flat with the frequency changing when $x \leq 0.02$ which means its have quite stable frequency dependence. When $x = 0.05$, both dielectric constant and dielectric loss decreases with the frequency increasing. This is a very common behavior of dielectric and ferroelectrics [16] related to leakage conductance. The decrease is rapid in low frequencies but becomes much slower in higher frequencies. This phenomenon takes place when the jumping frequency of the electric charge carrier cannot follow the alternation of applied ac electric field beyond a certain critical frequency (Table 2).

The temperature dependency of dielectric constant and loss of the substituted samples at selected frequencies are given in Fig. 4. Dielectric constant decreases and dielectric loss increases as V^{5+} ion substitution increases. Two kinds of behavior are shown when $x \leq 0.01$ and $\geq$0.02. When

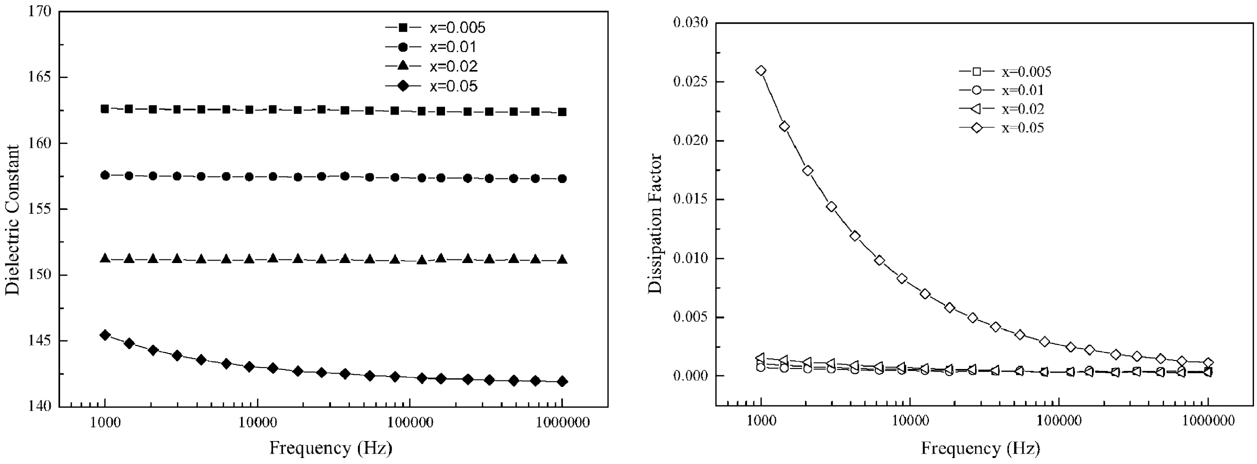

Fig. 3. Frequency dependency of dielectric constant and dissipation factor of $Bi_{1.5}Zn_{0.5}(Zn_{0.5}Nb_{1.5-x}V_x)O_7$ ceramics at room temperature.

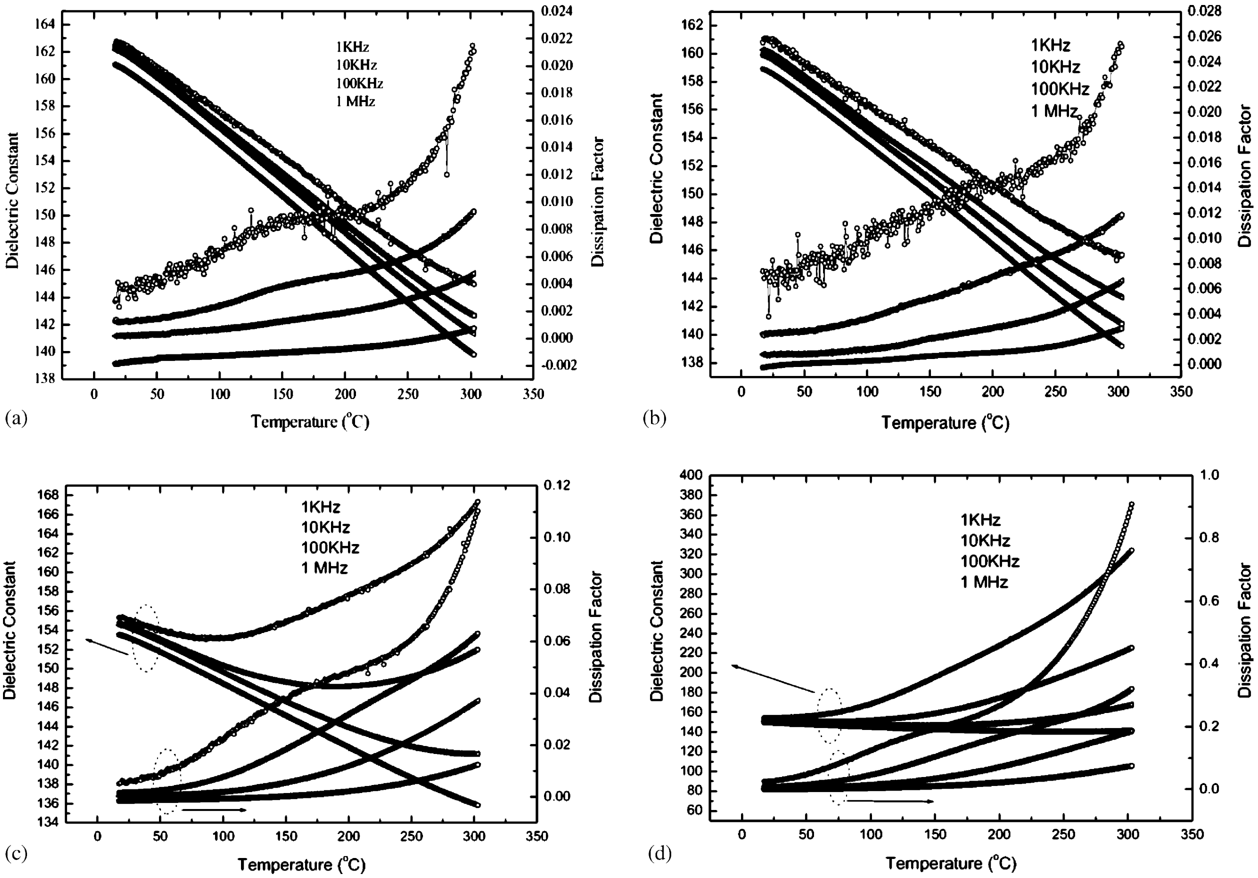

Fig. 4. Temperature dependency of dielectric constant and dissipation factor of $Bi_{1.5}Zn_{0.5}(Zn_{0.5}Nb_{1.5-x}V_x)O_7$ ceramics: (a) $x = 0.005$; (b) $x = 0.01$; (c) $x = 0.02$; (d) $x = 0.05$.

$x \leq 0.01$, the temperature dependency of dielectric constant diminishes continually and that of dielectric loss slightly increase with the temperature increasing. The dispersion of the dielectric constant and loss upon frequency and temperature was observed. No peaks in the dielectric constant curve were found as a function of frequency, which maybe considered to indicate that a lattice polarization-type phenomenon with dipole formation did not actually occur [17]. This dispersion may be associated to the presence of atomic defects in the structures. As to the pyrochlore case, one may assume that oxygen vacancies are a intrinsic defect. When $x \geq 0.02$, the dielectric constant and loss begin a rise with temperature increasing. The lower the frequency, the lower the onset point. This kind of dependence of ε and tan δ on temperature is typically associated with losses by conduction [18]. 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. Therefore, the dielectric polarization increases causing a marked increase in ϵ and tan δ as the temperature increases.

Table 2
The dielectric properties of $Bi_{1.5}Zn_{0.5}(Zn_{0.5}Nb_{1.5-x}V_x)O_7$ ceramics

Composition (x)	Density (measured) (g/cm^3)	Density (theoretical) (g/cm^3)	Relative density (%)	Lattice parameter (nm)
0	7.0175	7.1240	98.5	1.0552
0.005	7.0476	7.1202	99.0	1.0555
0.01	7.0056	7.1130	98.5	1.0556
0.02	6.9948	7.1083	98.4	1.0555
0.05	6.9219	7.1003	97.5	1.0547

4. Conclusions

The effect of V_2O_5 substitution on the process, structure and dielectric properties of Bi_2O_3–ZnO–Nb_2O_5 microwave ceramics were investigated. The V_2O_5 amount is in the direct proportion to the sintering temperature of the substituted sample with the lowered sintering temperature from 840 to 920 °C. With the small amount of V_2O_5 substitution ($0.005 \leq x \leq 0.05$), the phase structures still kept to be the pure cubic pyrochlores which means the V^{5+} is successful to be introduced to the B site. The dielectric constants of V_2O_5-substituted BZN ceramics decrease gradually from 162 to 147 while the temperature coefficients continuously increase from −520 to −348 ppm/°C with the substitution amount increasing. The dielectric loss are in smaller level as that of the basic composition at the smaller substitute amount ($x \leq 0.02$) but then degraded when the substitution reached to $x = 0.05$. The frequency and temperature dielectric spectroscopy reveal the dispersion on the dielectric constant and loss.

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