

Effect of Ca substitution on structure and dielectric properties of bismuth-based microwave ceramics

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Abstract The effect of the chemical substitution of Ca cation on the microstructure and microwave dielectric properties of bismuth-based pyrochlores has been investigated. Broad ranges of solid solutions based on $(\text{Bi}_{3x}\text{Zn}_{12-3x})(\text{Zn}_x\text{Nb}_{2-x})\text{O}_7$ ($x=0.56\text{--}0.64$) were obtained with Ca cation substitution of Zn at A site. The XRD patterns revealed that the substitution of Ca for Zn led to the α – β pyrochlore phase transformation and pure β pyrochlore structure were obtained. The dielectric constants (ϵ_r) varied slightly with x increasing. The quality factor Q was significantly improved by Ca substitution. The temperature coefficient of resonant frequency (τ_f) was negative and increased with x increasing. $(\text{Bi}_{3x}\text{Ca}_{2-3x})(\text{Zn}_x\text{Nb}_{2-x})\text{O}_7$ ($x=0.58$) ceramic, sintered at 960 °C, exhibits the optimal microwave dielectric properties of $\epsilon_r \sim 74$, Q value $\sim 6,457$ (at 4.8 GHz), and $\tau_f \sim -143$ ppm/°C.

Keywords Bismuth zinc niobate · Pyrochlore · Calcium-substitution · Dielectric properties

1 Introduction

Recently, many researchers have been focusing on developing dielectric materials with high quality factor (Q_f), high dielectric constant (ϵ_r) and zero temperature coefficient of resonant frequency (τ_f) for the use of dielectric resonator and microwave device substrate. High dielectric constant can effectively reduce the size of resonators since the wavelength in dielectrics is inversely proportional to $\sqrt{\epsilon_r}$ of the wave-

length in vacuum. Naturally, bismuth pyrochlore materials are good candidates due to their high dielectric constant and low dissipation factor and low temperature coefficient of resonant frequency with low sintering-temperatures.

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. Previous work revealed that there are two main phases in the system: a cubic pyrochlore phase (α phase) $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ ($\epsilon=150$, $\alpha_\epsilon \approx -400$ ppm/°C) and a monoclinic pyrochlore phase (β phase) $\text{Bi}_2\text{Zn}_{2/3}\text{Nb}_{4/3}\text{O}_7$ ($\epsilon=80$, $\alpha_\epsilon \approx +200$ 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 promising candidate for the application to low-firing high-frequency multilayer devices [4–6]. Hiroshi Kagata et al. [7] first researched the microwave property of Bi-based ceramics. But the Bi_2O_3 -CaO-ZnO- Nb_2O_5 system he reported has the poor Q factor ($\epsilon=79$, $Q=360$ (3.3 GHz), $\tau_f=+1$ ppm/°C).

Previous work reveals that the β phase pyrochlore ceramics have higher quality factor but lower dielectric constant compared to α phase pyrochlore ceramics [8]. In order to explore Bi-based pyrochlores with high dielectric constant and excellent microwave properties, we have focused on identifying new compositions through appropriate ion doping and substitution. The pyrochlore structure is one of the oxygen octahedron based family with a general formula of $\text{A}_2\text{B}_2\text{O}_7$ (space group $\text{Fd}\bar{3}\text{m}$, $Z=8$) [9]. The larger A cations are eightfold coordinated and are located in a scalenohedron. The smaller B cations are sixfold coordinated and are located an octahedron. In the

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BZN system, Bi^{3+} prefers to occupy A site due to its large radius (1.11 Å) and Nb^{5+} prefers to occupy B site due to its small radius (0.64 Å), whereas Zn^{2+} is distributed in both A site and B site due to its medium radius (0.75 Å) but prefers to enter B site first [10]. Considering the pure monoclinic BZN pyrochlore was only found in a very narrow region near $\text{Bi}_2\text{Zn}_{2/3}\text{Nb}_{4/3}\text{O}_7$ [4], so introducing Ca^{2+} (radius, 1.12 Å) to substitute Zn^{2+} in A site of $(\text{Bi}_{3x}\text{Zn}_{2-3x})(\text{Zn}_x\text{Nb}_{2-x})\text{O}_7$ will probably lead the α - β phase transformation to obtain a pure β phase.

In this study, the calcium ions were introduced into bismuth zinc niobate pyrochlore to form substitutional solid solutions by a solid reaction process. The influences of Ca^{2+} substitution on the phase evolution and dielectric properties of $(\text{Bi}_{3x}\text{Ca}_{2-3x})(\text{Zn}_x\text{Nb}_{2-x})\text{O}_7$ ($x=0.56$ – 0.64) were studied.

2 Experimental

The compositions of Bi-based composition $(\text{Bi}_{3x}\text{Ca}_{2-3x})(\text{Zn}_x\text{Nb}_{2-x})\text{O}_7$ $x=0.56$ – 0.64 were synthesized by conventional ceramic technology. The constituent oxides were weighed out in proper ratio and mixed with alcohol using zirconia milling media. The slurries were 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 12 mm in diameter and about 1 mm high. The discs were finally sintered from 900 to 980 °C for 2 h.

The X-ray diffraction patterns were obtained using a Rigaku D/MAX-2400 X-ray diffractometer with $\text{CuK}\alpha$ radiation with steps of 0.02° by the scanning rate $10^\circ/\text{min}$. The microstructure characterization was made by a scanning electron microscope (SEM). The apparent density is measured by Archimedes method.

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 microwave dielectric behavior was measured using Hakki–Coleman method and a $\text{TE}_{01\delta}$ resonant cavity method with 8720ES Network Analyzer. The temperature

coefficient of frequency is measured by shielded cavity with a DELTA 9023 Chamber.

3 Results and discussion

Table 1 showed that the resulting powder has good sinterability and relatively dense ceramics could be obtained easily at the temperature of 900–980 °C. The sintering temperature lowered and the density increased with the x increasing. The resistivity reaches the summit of $10^{14}\Omega\text{ cm}$ at $x=0.56$ but then decreases until $10^{11}\Omega\text{ cm}$ at $x=0.62$. The dielectric constant of various composition are all around 80 and gradually decrease with x increasing, and the dissipation factor are very low ($\tan\delta < 10^{-3}$) under low frequency at the room temperature.

3.1 Crystal structure

The XRD patterns of Ca-substituted BZN pyrochlore $(\text{Bi}_{3x}\text{Ca}_{2-3x})(\text{Zn}_x\text{Nb}_{2-x})\text{O}_7$ are showed in Fig. 1(a). The basic ceramics $(\text{Bi}_{3x}\text{Zn}_{2-3x})(\text{Zn}_x\text{Nb}_{2-x})\text{O}_7$ ($x=0.56$ – 0.64) exhibit cubic and monoclinic pyrochlore co-existing biphasic [2]. However, all the ceramics turn to pure β phase pyrochlore phase after Ca substitution, when x from 0.56 to 0.64. The structure comparison with unsubstituted BZN β phase is showed in the Fig. 1(b) and we can see the structure of $(\text{Bi}_{3x}\text{Ca}_{2-3x})(\text{Zn}_x\text{Nb}_{2-x})\text{O}_7$ ceramics are all pure β phase as that of $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$. It suggests that the Ca cation substitution of Zn in A-site led to the α - β phase transformation to form the pure monoclinic pyrochlore structure. This can be easily understand from the view of pyrochlore crystal chemistry and corresponds to the phase transition trend we revealed in BZN pyrochlores [11]. With the x increasing, the diffraction intensities of some diffraction lines increase (see the arrows marked).

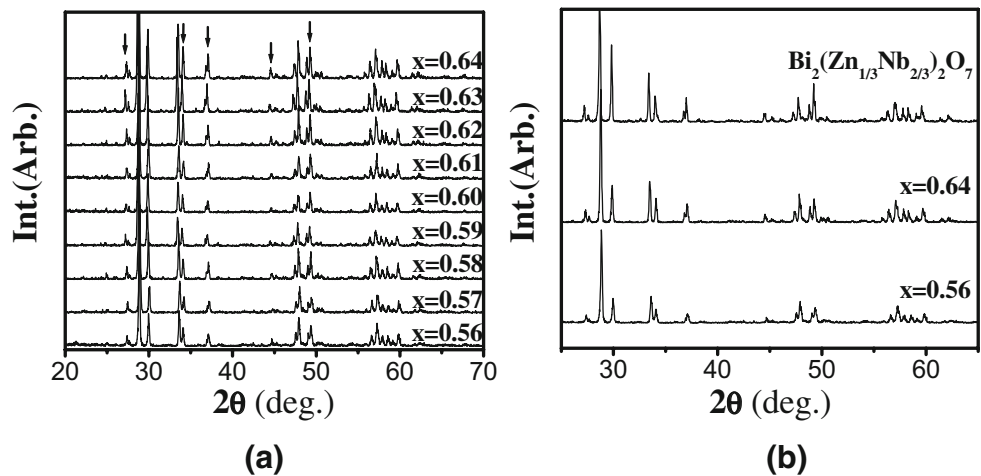
3.2 SEM analysis

The SEM of ceramics $(\text{Bi}_{3x}\text{Ca}_{2-3x})(\text{Zn}_x\text{Nb}_{2-x})\text{O}_7$ with various x values sintered at different temperatures are

Table 1 The sintering temperatures, densities and dielectric properties of $(\text{Bi}_{3x}\text{M}_{2-3x})(\text{Zn}_x\text{Nb}_{2-x})\text{O}_7$ ceramics.

Composition	x	ST (°C)	ρ ($\Omega\text{ cm}$)	Density (g/cm^3)	α_e (ppm/°C)	Microwave dielectric properties				τ_f (ppm/°C)
						ϵ_r	Q	f (GHz)	$Q \times f$ (GHz)	
M=Ca	0.56	980	4.0×10^{14}	7.053	322	75	1,393	3.64	5,076	-82
	0.58	960	4.4×10^{13}	7.204	300	74	1,349	3.84	5,182	-72
	0.6	960	6.1×10^{13}	7.326	276	71	1,128	3.74	4,219	-61
	0.62	940	4.9×10^{11}	7.334	228	74	1,298	3.78	4,903	-56
	0.64	920	2.5×10^{12}	7.427	205	76	870	3.95	3,440	-54
M=Zn	0.64	1000	3.6×10^9	7.516	105	75	459	3.83	1,755	-77

Fig. 1 XRD patterns of $(\text{Bi}_{3x}\text{Ca}_{2-3x})(\text{Zn}_x\text{Nb}_{2-x})\text{O}_7$ ceramic (a) $x=0.56\text{--}0.64$ (b) structure comparison with unsubstituted BZN β phase ($x=0.67$)



shown in Fig. 2. The SEM analysis reveal that the dense structure can be obtained after the substitution and the sintering temperature is as lower as $920\text{--}980^\circ\text{C}$. The grain size is about $1\text{--}3\ \mu\text{m}$ on average and increases with the sintering temperature.

3.3 Dielectric properties

The dielectric properties of the samples with different composition at microwave frequency are shown in Table 1. The apparent density increases, while the temperature

coefficients of dielectric constant (α_ϵ) decreases with x increasing. When x is from 0.56 to 0.64, the dielectric constants (ϵ_r) vary slightly. The Q factor reduces and temperature coefficient of frequency is negative and increasing with x increasing. When $x=0.58$, it exhibits the optimal microwave dielectric properties of $\epsilon_r \sim 74$, Qf value $\sim 6,457$ (at 4.8 GHz), and $\tau_f \sim -143\ \text{ppm}/^\circ\text{C}$. Compared to basic ceramic without substitution, the properties under microwave frequency improved remarkably as Qf increasing from 1,755 to 6,457. This improvement should be related to the Ca substitution which leads structure change

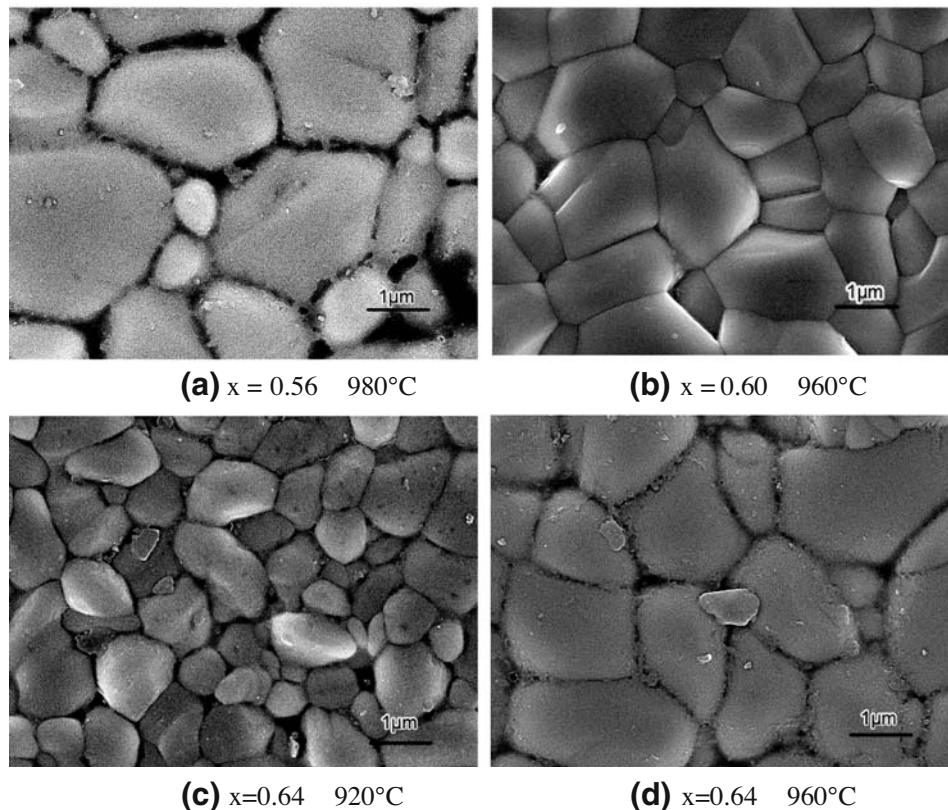


Fig. 2 SEM micrographs of $(\text{Bi}_{3x}\text{Ca}_{2-3x})(\text{Zn}_x\text{Nb}_{2-x})\text{O}_7$ ceramic (a–d)

to form pure β phase, thus avoid the deteriorated microwave dielectric properties from an anomalous dielectric relaxation in microwave range of the α phase [12].

4 Conclusion

The dielectric properties and the microwave dielectric properties of bismuth-based pyrochlores $(\text{Bi}_{3x}\text{Ca}_{2-3x})(\text{Zn}_x\text{Nb}_{2-x})\text{O}_7$ ($x=0.56\text{--}0.64$) have been investigated. The XRD patterns revealed that the substitution of Ca for Zn led to the α – β pyrochlore phase transformation and pure β pyrochlore structure were obtained. The dielectric constants (ϵ_r) gradually decreased with x increasing. The quality factor Q is significantly improved by Ca substitution. The temperature coefficients of resonant frequency (τ_f) increases with x increasing. $(\text{Bi}_{3x}\text{Ca}_{2-3x})(\text{Zn}_x\text{Nb}_{2-x})\text{O}_7$ ($x=0.58$) ceramics, exhibits the optimal microwave dielectric properties of $\epsilon_r \sim 74$, Qf value $\sim 6,457$ (at 4.8 GHz), and $\tau_f \sim -143$ ppm/ $^\circ\text{C}$.

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References

1. Z.P. Wang, S.Y. Zhang, *Electron. Compon. Mater. (Chin.)* **1**(1), 11 (1979)
2. X.L. Wang, H. Wang, X. Yao, *J. Am. Ceram. Soc.* **80**(10), 2745 (1997)
3. D. Liu, Y. Liu, S. Huang, X. Yao, *J. Am. Ceram. Soc.* **76**(8), 2129 (1993)
4. H. Wang, PhD thesis, The Xi'an Jiaotong University, 1998
5. H. Wang, X. Yao, *J. Mater. Res.* **16**(1), 83 (2001)
6. H. Wang, X. Wang, X. Yao, *Ferroelectrics* **195**, 19 (1997)
7. H. Kagata, T. Inoue et al., *Jpn. J. Appl. Phys.* **31**(Part1) (9B), L3152 (1992)
8. C.A. Randall, J.C. Nino, A. Baker, et al., *Am. Ceram. Soc. Bull.* **11**, 9106 (2003)
9. M.A. Subramanian, G. Aravamudan, G.V. Subba Rao, *Prog. Solid State Chem.* **15**, 55 (1983)
10. H. Wang, H.L. Du et al., *Mater. Sci. and Eng. B.* **99**, 20 (2003)
11. H. Wang, X. L. Wang, et al., *Proceedings II of the 10th IEEE International Symposium on Applications of Ferroelectrics* (East Brunswick, USA, Aug., 1996), pp. 787–790
12. S. Kamba et al., *Phys. Rev., B.* **66**, 054106 (2002)