

Phase Transformation Behavior of Bi₂O₃-ZnO-Nb₂O₅ Ceramics sintered at low Temperature

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Abstract

To co-fire with commercial LTCC (Low Temperature Co-fired Ceramic) materials at 850°C ~ 880°C, different contents of B₂O₃ were added to the Bi₂O₃-ZnO-Nb₂O₅ (BZN) ceramics. According to the test results, the cubic phase of BZN was transformed into orthorhombic in all the test materials. BiNbO₄ phase was formed in test materials with 2 ~ 5 wt% of B₂O₃ addition. The phase transformation of cubic BZN was controlled during the synthesis process with excess ZnO content. The Cubic and orthorhombic phases of BZN could coexist and be sintered densely at 850°C/2hr.

Keywords: BZN, LTCC, capacitor, dielectric properties

1. Introduction

Bi₂O₃-ZnO-Nb₂O₅ ceramics have been attracted much attention to be co-fired with LTCC materials due to its low sintering temperature.[1-2]. BZN ceramics possesses two phases. One is Bi₂Zn_{2/3}Nb_{4/3}O₇ and the other is Bi_{3/2}ZnNb_{3/2}O₇. Bi₂Zn_{2/3}Nb_{4/3}O₇ belongs to the Cubic Pyrochlore Phase (C-BZN). The dielectric constant temperature coefficient of C-BZN is ~ -400ppm/°C. Bi_{3/2}ZnNb_{3/2}O₇ belongs to the Pseudo Orthorhombic Phase (O-BZN). The dielectric constant temperature coefficient is ~ +200ppm/°C. Being the positive and negative dielectric constant temperature co-efficient, the NP0 (negative positive and near zero) spec of dielectric constant temperature coefficient could be obtained by a proper mixing of these two phases. In this paper, the flux of B₂O₃ is used to discuss the dielectric properties and phase transformation of BZN ceramics sintered at low temperatures.

2. Experimental and Results

The BZN ceramics are synthesized by two stages. The first synthesis process is to weigh ZnO and Nb₂O₅ by the stoichiometry of 4/3 and 2/3 mole ratio to obtain the C-ZN ceramic. 1 and 3/2 mole ratio of ZnO and Nb₂O₅ ceramics are weighed to obtain the O-ZN powder. The C-ZN and O-ZN powders are calcined in air at 1000°C for 4hrs respectively. The second synthesis process is to add the Bi₂O₃ ceramic to C-ZN and O-ZN powders to obtain the C-BZN and O-BZN materials by the stoichiometry mole ratio. The C-BZN and O-BZN powders were calcined in air at 800°C for 4hrs. 45.5g of C-BZN and 54.5g of O-BZN with 0.5wt% to 5 wt% of B₂O₃ flux are mixed in alcohol with 2mm Zirconia beads for 24hrs. Detail chemical composition and sample number is

listed in Table 1. After drying, the BZN powders are pressed uniaxially into pellets with 10 mm diameter and 1.65 mm thickness. The test materials are sintered at a temperature regime from 830°C to 930°C in air for 2 hrs. The sintered pellets are analyzed by x-ray. The micro-structure and fracture surface were observed by SEM.

Table 1. Sample number and chemical composition.

Sample number	Sintering Extra ZnO adding flux before C-ZN and O-ZN calcine process			
	C-BZN (g)	O-BZN (g)	B ₂ O ₃ (wt%)	O-ZN
B _{0.5} -BZN	45.5	54.5	0.5	-
B ₁ -BZN	45.5	54.5	1.0	-
B ₃ -BZN	45.5	54.5	3.0	-
B ₅ -BZN	45.5	54.5	5.0	-
Zn _{0.5} -B ₅ -BZN	45.5	54.5	5.0	0.5
Zn ₂ -B ₅ -BZN	45.5	54.5	5.0	2
Zn ₅ -B ₅ -BZN	45.5	54.5	5.0	5
Zn _{7.5} -B ₅ -BZN	45.5	54.5	5.0	7.5

Fig. 1 illustrates the x-ray diffraction of C-BZN and O-BZN. It shows that the pure cubic and pseudo orthorhombic pyrochlore phase are synthesized. No extra x-ray peak are found in the C-BZN and O-BZN with 7.5wt% of excess ZnO before C-ZN and O-ZN calcine. It implies the high solubility of Zn²⁺ ions in the C-ZN and O-BZN crystals [3]. Fig. 2 illustrates the x-ray diffraction of B_x-BZN materials sintered at 850°C. It shows that the cubic BZN phase disappeared (2θ~29.2°) in all the test materials. It reveals that the BiNbO₄ phase appeared in the B₂O₃ >2wt% materials. Fig. 3 illustrates the x-ray diffraction of Zn_y-B₅-BZN material sintered at 850°C. It shows that both the C-BZN and O-BZN phases could coexist in the BZN materials. The BiNbO₄ phase has disappeared.

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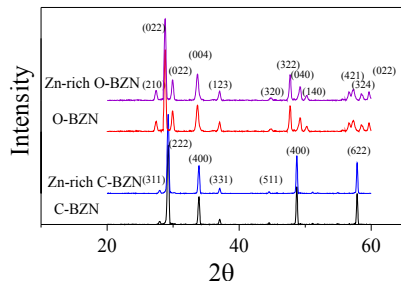


Fig. 1. X-ray diffraction of C-BZN and O-BZN.

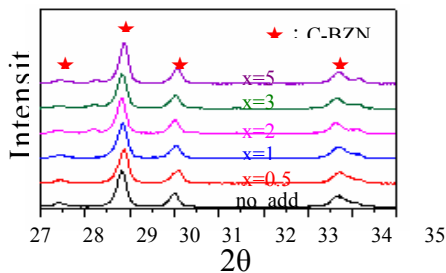


Fig. 2. X-ray diffraction of B_x -BZN materials sintered at 850°C.

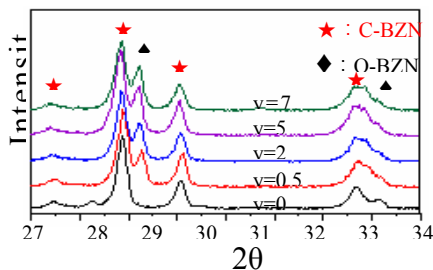


Fig. 3. X-ray diffraction of Zn_y-B_5 -BZN materials sintered at 850°C.

X-ray peaks of C-BZN ((022) plane) and O-BZN((222) plane) are integrated. The ratio of C-BZN integrated area and C-BZN plus O-BZN (C/C+O ratio) are illustrated in Fig. 4. It shows that the C/C+O ratio is not affected by sintering temperature.

Fig. 5(a) presents the correlation of dielectric constant and sintering temperature of B_x -BZN. It shows that the dielectric constant decreases with increasing B_2O_3 addition. For the Zn_y-B_5 -BZN materials, the correlation of dielectric constant and sintering temperature is presented in Fig. 5(b). It indicates that the dielectric constant is not affected by the B_2O_3 .

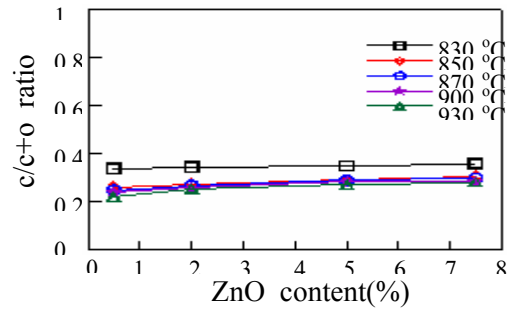


Fig. 4. correlation of C-BZN ((022) plane) integrated area / C-BZN + O-BZN((222) plane) integrated area and the ZnO content.

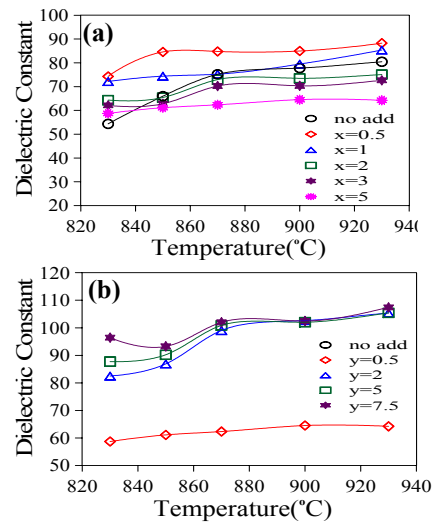


Fig. 5. Correlation of dielectric constant and sintering temperature of (a) B_x -BZN, (b) Zn_y-B_5 -BZN materials.

3. Summary

The firing of mixed C-BZN and O-BZN ceramics with B_2O_3 flux would lead to the transformation of C-BZN to O-BZN. The excess Zn^{2+} ions solved in the C-BZN could suppress transformation.

4. References

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