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 Bi2Zn2/3Nb4/3O7 and the other is Bi3/2ZnNb3/2O7. Bi2Zn2/3Nb4/3O7 belongs to the Cubic Pyrochlore Phase (C-BZN). The dielectric constant temperature coefficient of C-BZN is ~ -400 ppm/°C. Bi3/2ZnNb3/2O7 belongs to the Pseudo Orthorhombic Phase (O-BZN). The dielectric constant temperature coefficient is ~ +200 ppm/°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 5 wt% of B2O3 flux were 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 were analyzed by x-ray. The micro-structure and fracture surface were observed by SEM.

Table 1. Sample number and chemical composition.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>C-BZN (g)</th>
<th>O-BZN (g)</th>
<th>B2O3 (wt%)</th>
<th>O-ZN calcine process</th>
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<tr>
<td>B0.5-BZN</td>
<td>45.5</td>
<td>54.5</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>B1-BZN</td>
<td>45.5</td>
<td>54.5</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>B3-BZN</td>
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<td>54.5</td>
<td>3.0</td>
<td>-</td>
</tr>
<tr>
<td>B5-BZN</td>
<td>45.5</td>
<td>54.5</td>
<td>5.0</td>
<td>-</td>
</tr>
<tr>
<td>Zn0.5-B5-BZN</td>
<td>45.5</td>
<td>54.5</td>
<td>5.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Zn2-B5-BZN</td>
<td>45.5</td>
<td>54.5</td>
<td>5.0</td>
<td>2</td>
</tr>
<tr>
<td>Zn5-B5-BZN</td>
<td>45.5</td>
<td>54.5</td>
<td>5.0</td>
<td>5</td>
</tr>
<tr>
<td>Zn7.5-B5-BZN</td>
<td>45.5</td>
<td>54.5</td>
<td>5.0</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Fig. 1 illustrates the x-ray diffraction of C-BZN and O-BZN. It shows that the pure cubic and pseudorhombohedral pyrochlore phase coexisted. No extra x-ray peak was found in the C-BZN and O-BZN with 7.5wt% of excess ZnO before C-ZN and O-ZN calcine. The cubic BZN phase was disappeared (20 ~ 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 Zny-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.
Fig. 1 illustrates the x-ray diffraction of C-BZN and O-BZN. It shows that the pure cubic can transform to a pseudoorthorhombic pyrochlore phase after synthesis. No extra x-ray peaks are found in the C-BZN and O-BZN with 7.5wt% of excess ZnO before calcination. It implies that the Zn^{2+} ions can dissolve in the C-ZN and O-ZN crystals [3]. Fig. 2 illustrates the x-ray diffraction of B_{x}-BZN material sintered at 850°C. It shows that the cubic BZN phase disappeared (2\theta \sim 29.2°) in all the test materials. It reveals that the BiNbO_4 phase appeared in the B_2O_3 >2wt% materials. Fig. 3 illustrates the x-ray diffraction of Zn_{y}-B_{5}-BZN materials sintered at 850°C. It shows that both the C-BZN and O-BZN phases could coexist in the BZN materials. The BiNbO_4 phase has disappeared.

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.

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