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Dielectric properties of B_2O_3-doped $BiNbO_4$ ceramics

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Abstract

The densified B_2O_3-doped $BiNbO_4$ ceramics were obtained after sintering at 960 °C. The dielectric properties of B_2O_3-doped $BiNbO_4$ ceramics were studied. Samples sintered in air show low frequencies (from 1 to 100 kHz) dielectric relaxation behaviors at about 150 °C. The dielectric relaxation temperature would decrease when the sample was sintered in N_2. The dielectric constant and loss at low frequencies increased rapidly and the microwave dielectric properties deteriorated with increasing B_2O_3 content when sintered in N_2. The dielectric constant, Q-value and TCF-value of the 0.4 wt.% B_2O_3-doped $BiNbO_4$ ceramic at 4.8 GHz are 41.5, 4400 and -2.4 ppm/°C, respectively. A defect model was proposed for the explanation of dielectric behavior of B_2O_3-doped $BiNbO_4$ ceramics.

Keywords: B. Defect; C. Dielectric properties; $BiNbO_4$ ceramic

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1. Introduction

Multilayer devices have been developed to reduce the size of microwave devices in telecommunication system. Low temperature co-fired dielectric ceramics have been intensively studied for these applications. A $BiNbO_4$ ceramic material with low sintering temperature is suitable for microwave resonators and filters. But it was difficult to densify $BiNbO_4$ without a sintering aid. CuO, V_2O_5 or CuO–V_2O_5 mixtures as a sintering aid used to densify the $BiNbO_4$ ceramics have been widely studied [1–4]. These works showed $BiNbO_4$ ceramic is a good candidate for low firing microwave ceramic. But dielectric behaviors related to frequencies and temperatures have not been studied. The dielectric loss of ionic crystal has been extensively studied at low frequencies ($\leq$1 MHz) [5] and high frequencies ($\geq$30 GHz) [6]. However there still does not exist a quantitative, experimentally verified theory describing dielectric loss in the microwave band. In this work, low frequency dielectric relaxation behaviors and microwave dielectric properties of B_2O_3-doped $BiNbO_4$ ceramics were investigated. A defect pair model was proposed and effects of defects on dielectric properties were discussed.

2. Experiment procedures

Specimen powders were prepared by conventional solid-state reaction process. Proportional amounts of starting materials of Bi_2O_3 and Nb_2O_5, according to the composition of $BiNbO_4$, with B_2O_3 as a sintering aid were mixed for 24 h in a nylon jar using ZrO_2 media. Mixed powders were dried and calcined at 800 °C for 2 h, then they were remilled for 24 h with PVA solution as a binder. They were pressed into pellets and then sintered at about 960 °C for 2 h.

The microstructure observation of the sintered ceramics was preformed by SEM (JOEL, 5510LV). The crystalline phase of sample was identified by XRD (BRUKER, D8). The bulk density of sample was measured by the Archimedes' method. Dielectric properties at low frequency were measured by HP4284. The dielectric constant and the quality value Q at approximately 5 GHz were measured using the Hakki–Coleman [7] dielectric resonator methods. The $TE_{01\delta}$ mode was examined using a vector network analyzer (HP8753E). The temperature coefficient of resonant frequency was obtained by measuring $TE_{01\delta}$ resonant frequency at 20 and 80 °C, respectively. The temperature coefficient of resonant frequency was defined as follows:

$$\mathrm{TCF} = \frac{f_{80} - f_{20}}{60 \times f_{20}} \times 10^6\ \mathrm{ppm/^\circ C} \quad (1)$$

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3. Results

$BiNbO_4$ ceramics doped with x wt.% B_2O_3 (where $x = 0.4$, 0.6 and 0.8, respectively) sintered at 960 °C for 2 h exhibited single orthorhombic phase without any second phase determined by XRD. The density of the samples is 97% of theoretical density. Fig. 1a–c show the dielectric constant, *Q*-value and TCF-value at about 4.8 GHz and room temperature as a function of the amount of B_2O_3 dopant of the samples sintered in air. When the amount of B_2O_3 increases, the dielectric constant decreases from 41.5 to 39.6 and *Q*-value decreases from 4400 to 517. The *Q*-value decreases from 4400 to 500 while the sample was sintered in N_2 for $x = 0.4$ (*Q*-value cannot be measured for $x = 0.6$ and 0.8). This may be related to a presence of defects discussed in following section. The TCF decreased with the increase of B_2O_3 content. The TCF-value of −2.4 ppm/°C was obtained at $x = 0.4$.

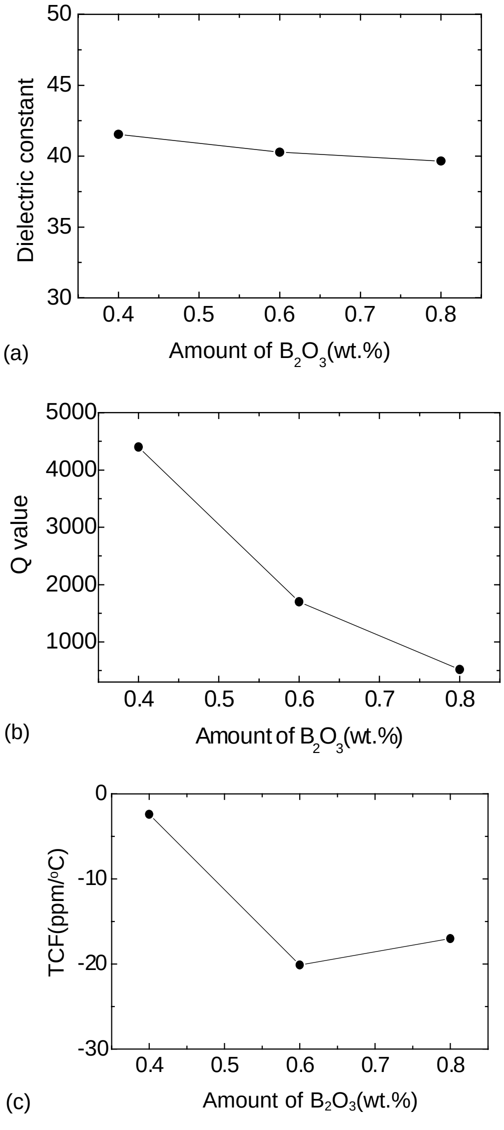

Fig. 1. The microwave dielectric properties of B_2O_3-doped $BiNbO_4$ ceramics sintered in air: (a) dielectric constant, (b) *Q*-value and (c) TCF-value.

The temperature dependence of dielectric properties was measured from 20 to 500 °C in a frequency range of 1–100 kHz. For samples sintered in air, the temperature and frequency dependence of dielectric constant and dielectric loss is showed in Fig. 2a–c. Two sets of peaks were observed. The first peak occurred at a temperature about 150 °C, and the other occurred at above 350 °C. At the first peak, the dielectric constant and dielectric loss increase with the amount of B_2O_3 content. The dielectric constant is 48, 70 and 300 for $x = 0.4$, 0.6 and 0.8 wt.%, respectively at 1 kHz. It can be clearly seen that the maximum of the dielectric loss shifted to higher temperatures with the increase of frequency. Both the maximum of dielectric constant and dielectric loss increase, and the dielectric relaxation behavior is more apparent with the increase of B_2O_3 content. The activation energy of dielectric relaxation is 1.08–1.1 eV. At around room temperature the dielectric constants are very close for samples with different amount of B_2O_3. However, the dielectric constant increases from 48, 70 and 300 at about 150 °C. At the second peak, the maximum of dielectric constant is 290, 310 and 1134, respectively, the temperature for the maximum of the dielectric constant is 470, 407 and 397 °C, respectively for $x = 0.4$, 0.6 and 0.8 at 1 kHz, and the dielectric loss increases rapidly. This means that a new polarization factor appears above 100 °C.

When the sample was sintered in N_2, the first peak is at about 116 °C and the maximum of dielectric constant is 505 at 1 kHz, which are showed in Fig. 2d. The dielectric relaxation behavior appears at the first peaks, and the activity energy is 0.85 eV that is smaller than that of the sample sintered in air. The second peak is at about 223 °C, the maximum of dielectric constant is 1874. The temperature for the maximum of the dielectric constant decreases, the maximum of dielectric constant and dielectric loss increase in comparison with the sample sintered in air at the first peak and the second peak.

4. Discussions

The melting point of B_2O_3 is 460 °C and Bi_2O_3–B_2O_3 can form low temperature phase [8], so little amount of B_2O_3 is able to densify the ceramic. The 0.4-wt.%-B_2O_3-doped $BiNbO_4$ ceramic sintered at 960 °C for 2 h has a good microwave dielectric properties. The dielectric constant, *Q*-value and TCF-value are 41.5, 4400 and −2.4 ppm/°C, respectively. When the amount of B_2O_3 increases or the sample is sintered in N_2, the *Q*-value of ceramics decreases dramatically. The dependence of dielectric properties on temperature at low frequency has shown that the dielectric relaxation behavior related to defects will affect the microwave dielectric properties of the ceramics.

Because of the reaction between Bi_2O_3 and B_2O_3, bismuth vacancies V_{Bi}''' created in $BiNbO_4$ structure [8]. In

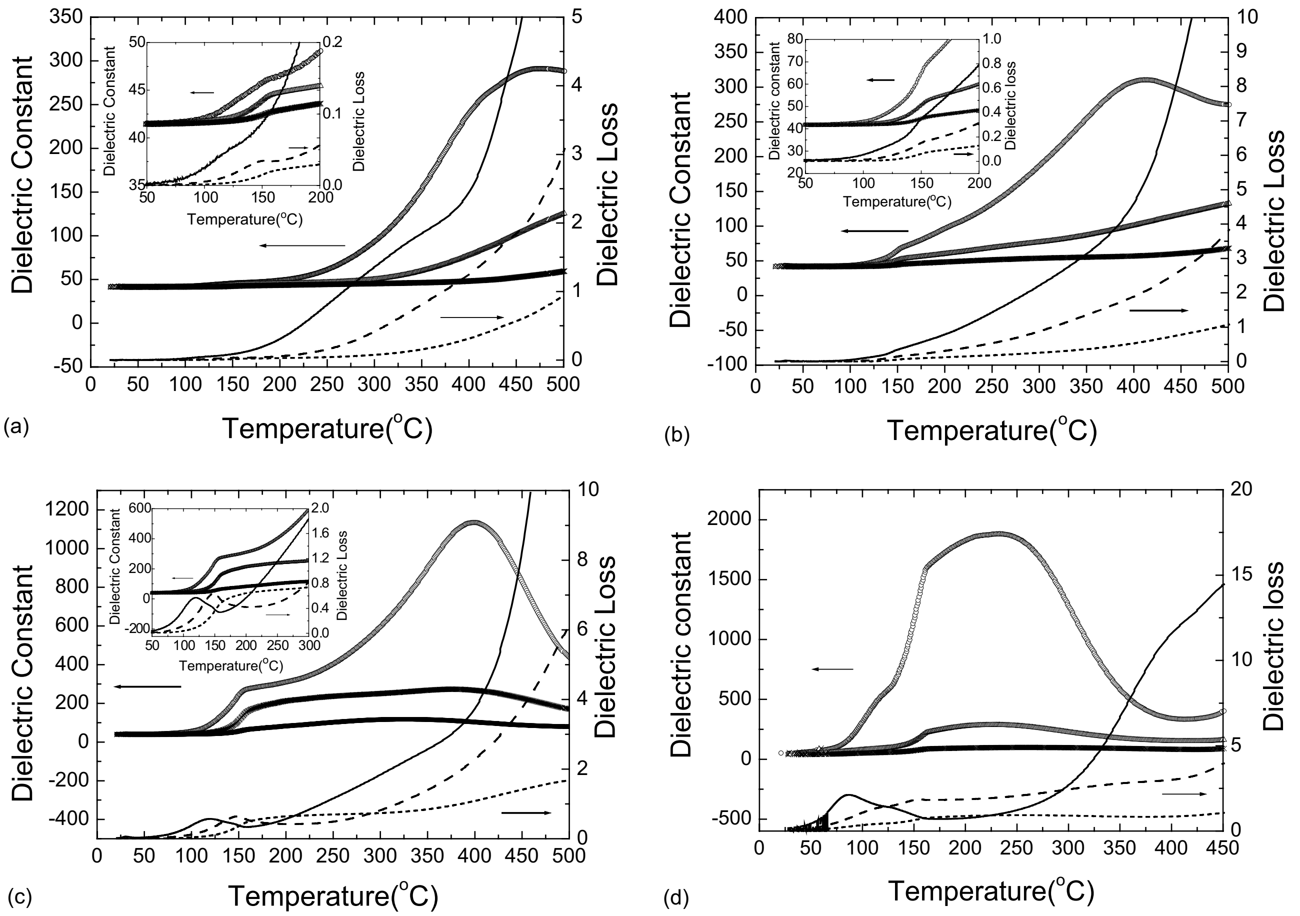

Fig. 2. Temperature dependence of dielectric constant and loss of *x*-wt.%-B_2O_3-doped $BiNbO_4$ ceramics: (a) $x = 0.4$, (b) $x = 0.6$, (c) $x = 0.8$ (sintered in air) and (d) $x = 0.4$ (sintered in N_2) at 1, 10 and 100 kHz (from top to bottom).

order to keep electrical neutrality, oxygen vacancies $V_{O}^{\cdot\cdot}$ must appear to balance the local negative charge of Bi vacancies [9]. The expression for charge neutrality is $2[V_{Bi}^{'''}] = 3[V_{O}^{\cdot\cdot}]$. Because of Coulomb force, the negatively charged vacancies and positively charged vacancies tend to attract each other forming coupled defects [9]. The combination of $V_{Bi}^{'''}$ and $V_{O}^{\cdot\cdot}$ forms defect pair (associate) such as $(2V_{Bi}^{'''} - 3V_{O}^{\cdot\cdot})$ that can be treated as a dipole. At low temperatures, the charged defect is bound into neutral associates and decreases the concentration of mobile charge carriers [9]. Based on the standpoint of the universal theory of polarization [10], the relaxation process, characterized by a loss peak behavior, occurs primarily in dipole-like system. When an external electric field is applied, the dipoles will be reoriented with the same frequency as the applied field but will lag behind out of phase. From the experimental results, the dielectric relaxation at the first peak can be related to the dipole $(2V_{Bi}^{'''} - 3V_{O}^{\cdot\cdot})$ under ac fields. When B_2O_3 content increases, the concentration of defect pairs increases, the dielectric constant will increase rapidly at 1 kHz, and the dielectric relaxation behavior is more apparent (relaxation activation energy decreases), especially for the samples sintered in N_2. In this case, there are more oxygen vacancies. The dielectric relaxation is not observed below 100 °C. This is due to the strong Coulomb force and the high activation energy of the defect pair resulting from the highly charged defect. Above 100 °C, the defect dipoles can be activated. The dielectric relaxation behavior will appear. With the increase of temperature, the defect associates will dissociate and form a number of thermal ions. In this case, the polarization of thermal ions is dominant. The dielectric constant increases and dielectric loss resulted from dissociation ionic conductivity increases rapidly, especially for the sample sintered in N_2. The possibility of thermal dissociation and temperature of thermal dissociation decrease with the increase of the concentration of defects. When the concentration of defect pairs is lower, the time constant of the coupled defects that is related to the activation energy is higher and defect pairs cannot respond to the external electric field at microwave frequency. So at room temperature, the defect pair has small effect on the dielectric loss at microwave frequency, even less than that at below 1 MHz. While the concentration of defect pairs increases, the crystal lattice will distort and the ionic conductivity increases. These will result in the high microwave dielectric loss. The TCF-value can be related to the distortion of crystal lattice.

5. Conclusions

The dielectric properties of B_2O_3-doped $BiNbO_4$ ceramics were examined. The dielectric constant, *Q*-value and TCF-value of samples sintered in air are 41.5, 4400 and −2.4 ppm/°C, respectively at about 4.75 GHz. When the amount of B_2O_3 addition increases or the sample was sintered in N_2, the *Q*-value decreases dramatically. The temperature dependence of dielectric properties demonstrated two sets of dielectric peaks at frequencies from 1 to 100 kHz. The dielectric constant and dielectric loss increase rapidly at these peaks. The dielectric relaxation behavior appeared at first peak. The formation of defect pair $(2V_{Bi}''' - 3V_{O}^{\cdot\cdot})$ was suggested to explain this phenomenon. The polarization of thermal ions is dominant at second peak. The increase in concentration of defect pairs will result in the distortion of crystal lattice, so the microwave dielectric properties deteriorate.

Acknowledgements

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