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Layered complex structures of $Bi_2(Zn_{2/3}Nb_{4/3})O_7$ and $BiNbO_4$ dielectric ceramics

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Abstract

The layered complex structures of $Bi_2(Zn_{2/3}Nb_{4/3})O_7$ (β-BZN) and $BiNbO_4$ ceramics have been designed by piling-up and cofiring. The adjustable dielectric constants and quality values of complex were obtained. The cofiring of β-BZN and $BiNbO_4$ ceramics was firstly attempted, and the sintered interface was observed by the scanning electron microscopy (SEM). The measured and calculated dielectric properties results of the layered complex were compared in detail, and have small relative errors at a frequency range of 100 Hz–1 MHz regions and microwave regions.

Keywords: Layered complex; BZN; $BiNbO_4$; Microwave dielectric properties

1. Introduction

Multilayer microwave devices have been developed to reduce the size of microwave devices in mobile radio communication systems. The microwave dielectrics with low sintering temperature (below 1000 °C) are needed to cofire with low loss conductors and low melting-point electrode such as silver and brass. The layered complex materials and cofiring between several kinds of dielectrics are also an effective method to get some new structures and new properties.

It is well known that Bi_2O_3–ZnO–Nb_2O_5 based dielectric ceramics were low-firing temperature materials, and had been studied for piezoelectric materials or multiplayer ceramic capacitors [1]. Both $Bi_2(Zn_{2/3}Nb_{4/3})O_7$ (β-BZN) and $BiNbO_4$ ceramics were the very popular studied microwave dielectric ceramics in recent years [2,3]. Both pure β-BZN and modification composition substituted by V^{5+} for Nb^{5+} could be densified at about 900 °C with dielectric constant $\varepsilon_r = 76$, Q-value = 800–900, and resonant frequency temperature coefficient τ_f is about −100 ppm °C [2,4]. α-$BiNbO_4$ ceramics doped with V_2O_5 also could be densified at about 900 °C with dielectric constant $\varepsilon_r = 43$, Q-value = 2500, and resonant frequency temperature coefficient τ_f is between 0 and +10 ppm °C [5]. The layered dielectric structures of different kinds of dielectrics could be obtained by piling up, cofiring, and agglutinating [6,7] and the dielectric properties could be modified by the layered structures.

In this work, the layered complex structures of β-BZN and $BiNbO_4$ ceramics are designed and prepared to obtain the low loss dielectric ceramics with adjustable dielectric constants and near-zero temperature coefficients. Both piling up and cofiring were used to obtain the layered structures. The measured results and the calculated results of the dielectric properties were compared and discussed.

2. Experimental

The $Bi_2(Zn_{2/3}(Nb_{4/3-0.002}V_{0.002}))O_7$ (β-BZN) and $Bi(Nb_{0.992}V_{0.008})O_4$ (BNV) powders were synthesized by the solid state reaction process. Then the flakes and cylinder samples were formed with 5 wt.% PVA binder with β-BZN, BNV, and different ratios of their mixtures, respectively. Several ratios of β-BZN to BNV ceramics were chosen for the layered structure as shown in Fig. 1. The layered structure of β-BZN and BNV ceramics could be well sintered at 900 °C because of their similar densified temperature, and similar shrinkage ratio. To measure the microwave properties of piling-up layers, the β-BZN, and BNV were sintered at 900 °C, and well polished to avoid the influence from air gaps.

Scanning electron microscopy (SEM, JEOL JSM-6460, Japan) and EDS observation were carried out on the fractured surfaces. The dielectric constant and dielectric loss at room temperature were measured by an LCR meter (HP4284A) from 100 Hz to 1 MHz using cofired pellets printed with silver electrode.

Dielectric behaviors at microwave frequency were measured by the $TE_{01\delta}$ shielded cavity method [8]. An 8720ES network analyzer was used for the microwave measurement.

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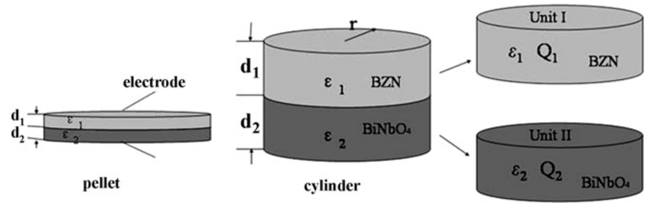

Fig. 1. The layered structure of BZN and $BiNbO_4$.

The resonant frequencies temperature coefficients τ_f were measured with the 8720ES network analyzer and a DELTA 9023 chamber using the $TE_{01\delta}$ shielded cavity method. The τ_f value was calculated by the formula

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25} \times (85 - 25)}, \tag{1}$$

where f_{85} and f_{25} were the $TE_{01\delta}$ resonant frequencies at 85 and 25 °C, respectively.

The calculated results were derived as following. The layered complex dielectric structures just correspond to capacitive elements in series and the inverse capacitances are additive, that is,

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} \tag{2}$$

The temperature coefficient of resonate frequency can be derived as

$$\tau_\varepsilon = \frac{1}{\varepsilon_r}\frac{d\varepsilon_r}{dT} = \varepsilon_r \sum_i r_i \frac{\tau_{\varepsilon_i}}{\varepsilon_i} \tag{3}$$

Considering the formula:

$$\tau_f = -\frac{1}{2}\tau_\varepsilon + \alpha_l \approx -\frac{1}{2}\tau_\varepsilon \tag{4}$$

where α_l is the thermal expansion coefficient, which is less than +10 ppm °C for ceramics, and could be neglected.

3. Results and discussion

Fig. 2 shows the SEM photos of boundaries of the layered complex cofired at 900 °C. The part of β-BZN and BNV has been sintered well, respectively but a narrow gap and pervasion are observed near the interfaces. The grains of β-BZN grew well with grain size of 0.6–3 μm, but secondary grain growth of $BiNbO_4$ was observed with the grain size more than 10 μm. The narrow gap, pervasion, and the big difference of grain size might have some harm to the dielectric properties of the layered complex at microwave regions. Macroscopically cracks besides the interface were caused because of the different shrinkage of β-BZN and $BiNbO_4$. So the perfect-layered cylinders samples couldn't be obtained by cofiring. But the cofired flake samples could be got with only a little bend but no cracks.

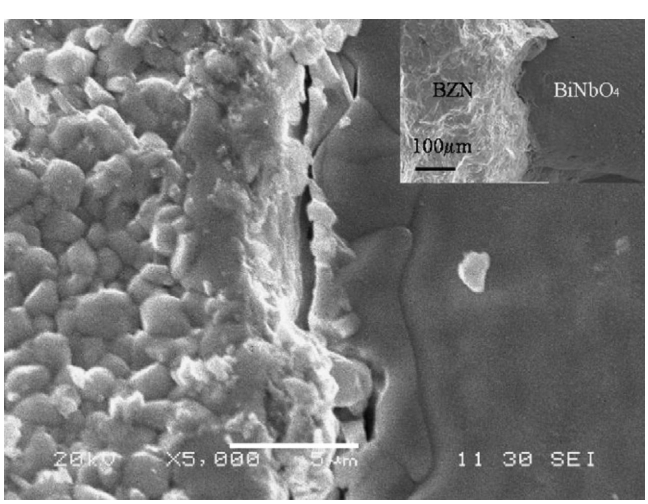

Fig. 2. SEM photo of boundary of the layered complex sintered at 930 °C.

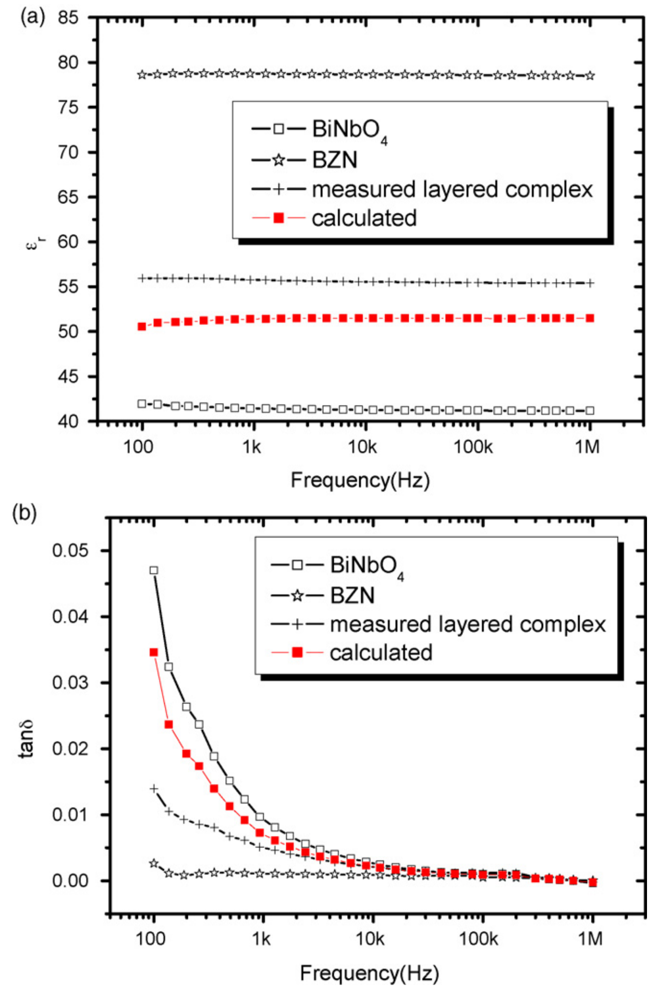

Fig. 3. Dielectric constant (a) and dielectric loss (b) of the layered complex at low frequency region.

Fig. 3 shows the dielectric properties of samples between frequency regions 100 Hz–1 MHz. The dielectric constants ε_r of all samples keeps nearly constant at this frequency range. The measured ε_r is about 76 for $Bi(Zn_{2/3}Nb_{4/3})O_7$ ceramics, 43 for $BiNbO_4$ ceramics, and 56 for the layered complex. And the calculated value for the layered complex using formula is about 51 as shown in Fig. 3(a). The relative error is about 9%. The dielectric loss is relative high at low frequency of $BiNbO_4$ ceramics because of the conductive loss. But the conductive loss of BZN is lower than $BiNbO_4$ ceramics. So the layered complex should also have low conductive loss at low frequency as shown in Fig. 3(b). Although the calculated results are higher than the real results at low frequencies (below 10 kHz) but both correspond well at relative high frequencies (10 kHz–1 MHz).

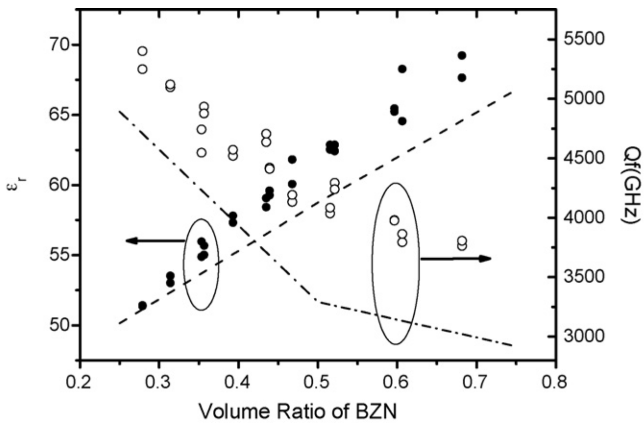

Fig. 4. Dielectric constants and Qf as a function of volume ratio of β-BZN for samples piling up (○, ●) and cofired samples (dash).

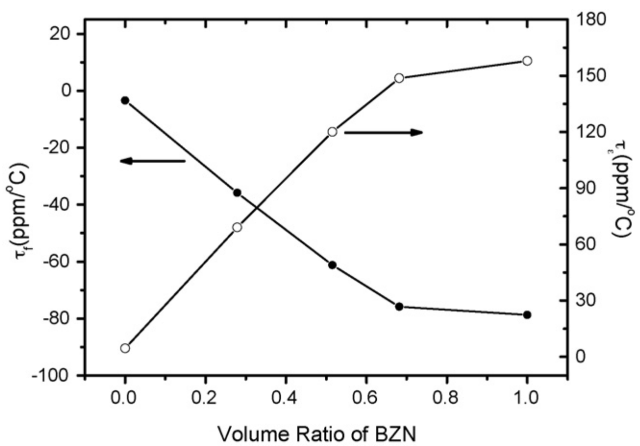

Fig. 5. Temperature coefficients of resonant frequency and dielectric constant as a function of volume ratio of β-BZN for samples piling up.

Fig. 4 shows the dielectric properties of samples with different ratio of β-BZN and $BiNbO_4$ at microwave frequencies region prepared both by piling up and cofiring. For piled up samples, the dielectric constant ε_r increased from 51.4 to 69.2 as the ratio of BZN increased from 0.28 to 0.68. The Qf values decreased from 5400 GHz at ratio = 0.28 to 3762 GHz at ratio = 0.68. The good properties were got at ratio = 0.48 with $\varepsilon_r = 61.8$, and Qf = 4192 GHz. For the cofired samples, both the ε_r and Qf values were a little smaller than that of the piled up samples. It is mostly attributed to the air gap and cracks ($\varepsilon_r = 1$) in the samples. The microwave properties were deteriorated seriously because of the cracks. So the cofiring between two kinds of materials with different shrinkage is not proper. The cofired cylindrical samples were got with many cracks, while flake samples with a little bend.

Fig. 5 shows the temperature coefficients of resonant frequency and dielectric constant of the layered complex as a function of volume faction of β-BZN. The τ_f of pure $BiNbO_4$ ceramics is −3.4 ppm °C and that of β-BZN ceramics is −78.7 ppm °C. The theory relationship calculated from formula between τ_f and volume ratio is nearly linear but the measured results are generally bigger than the theory value in negative direction. This might be caused by the narrow gap at the boundaries of the two phases, and needed to be studied further. The temperature coefficients of dielectric constant τ_ε changed from near zero to +162 ppm °C as the volume ratio of BZN increased from 0 to 1 at microwave regions. The adjustable τ_f and τ_ε could be obtained by adjusting the volume ratio.

4. Conclusions

The layered complex structures of β-BZN and $BiNbO_4$ ceramics have been designed by piling up and cofiring. Adjustable dielectric constants and quality values could be got in the layered complex by adjusting the volume fraction of β-BZN. The calculated results and the measured results were compared, and good correspondence was shown. The cofiring of β-BZN and $BiNbO_4$ ceramics are firstly attempted. Although the cofiring between bulk ceramics is not ideal, this might be beneficial to the development for their potential application in microwave and LTCC devices. The complex piled up showed better properties than that cofired. If a good pastern with low loss were used, the piling-up complex would play a more and more important role in microwave field.

Acknowledgements

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