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Dielectric properties of $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ electroceramics and thin films

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Abstract

Dielectric response of $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$, BiZN, ceramic materials and thin films were examined, for the first time, compared directly using terahertz (THz) spectroscopy. In the preparation of the ceramic materials, the two-step process exhibits a marked advantage over the one-step process in that the ceramic material's characteristics are relatively insensitive to the sintering parameters. The ceramic materials can achieve high density (7.2 g/cm^3), large dielectric constant ($K=67$), high quality factor ($Q\times f\cong 80{,}000$ GHz) and small temperature coefficient of resonance frequency ($\tau_f\cong -6$ ppm/°C), when processed at optimized sintering temperature (1050°C, 4 h). Crystalline BiZN thin films, can be easily obtained when the films were in-situ deposited at high enough substrate temperature 450–600°C (30 min). The dielectric constant of BiZN thin films in THz frequency regime, $(\varepsilon')_{f\cdot THz}=32$, is markedly smaller than the $(\varepsilon')_{b\cdot THz}$ value of BiZN bulk materials, and the quality factor of the thin films is less than 20% of the bulk materials.

Keywords: Dielectric properties; Films; Microwave ceramics

1. Introduction

Among the microwave dielectrics, $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ series materials exhibit marvellous properties such as high dielectric constant, low dielectric loss and adjustable temperature coefficient of resonance frequency and, most of all, need lower temperature for sintering. Microwave dielectric thin films possess overwhelming advantage over bulk materials in several aspects, including (1) lower operation voltage, (2) faster response and nonlinear relationship in dielectric properties,[1,2] which increases the tunability of the devices. Therefore, applications of these thin films as planar capacitors, coplanar waveguide, tunable phase shifter, tunable mixers and tunable filters have been extensively investigated.[3,4]

Dielectric properties of thin films are usually inferior to those of bulk materials with the same composition. To understand such a phenomenon, comparing the dielectric properties of the two forms of materials at the same operating frequency is necessary. Terahertz (THz) coherent radiation, time domain spectroscopy (THz–TDS) has become a powerful tool for studying the dielectric properties of materials in the region of the electromagnetic spectrum that is not easily accessible.[5,6] THz–TDS technique is thus adopted in this paper to study the dielectric properties of thin films and bulk BiZN materials.

2. Experimental methods

Two processing routes were utilized, for synthesizing BiZN bulk ceramics of the composition 80.8 mol% BiZN and 19.2 mol% ZN (BiZN–ZN), which possess zero τ_f value, they are (i) the one-step process: the Bi_2O_3, ZnO and Nb_2O_5 of the same composition as BiZN–ZN were mixed, pelletized and then, directly sintered at 1000–1200°C for 4 h; (ii) the two-step process: the BiZN and ZN materials were separately precalcined at 750°C for 4 h and 1000°C for 4 h, respectively, followed by mixing of the two powders to result in a mixture of the BiZN–

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ZN composition. The green pellets made of the BiZN–ZN powders were then sintered at 1000–1200°C for 4 h. The density of thus obtained pellets was measured using Archimedes technique. The BiZN thin films were prepared by pulsed laser deposition (PLD) technique,[7] using a pulsed XeCl excimer laser ($\lambda = 308$ nm, Lambda Physik) with an energy density of 3 J/cm^2. The films were deposited at 400–600°C in 0.1 mbar oxygen pressure (P_{O2}), followed by 10 min of annealing at the depositing temperature under 1 atm P_{O2}. MgO [100] substrates were used for growing the thin films.

The phase constituent and microstructure of the sintered materials were examined using X-ray diffractometer (Rigaku, Dmax/IIB). The microwave dielectric properties of the bulk ceramic materials were measured by a cavity method using H. P. 8722 network analyzer. In terahertz spectroscopy, a mode-locked Ti:Sapphire laser of 770 nm wavelength with 600 mW average output power generates sin100 fs pulses at a 76 MHz repetition rate. A large aperture photoconducting antenna is used as THz transmitter in our THz spectrometer. The transmitter consists of a semi-insulating GaAs wafer with two electrodes (AuGe) separated by about 500 μm and were biased at 100 V. Illuminating the area between the two electrodes with focused ultrashort laser pulses produces synchronous bursts of THz transient. The THz beam is collected and reflected by an off-axis paraboloidal mirror. The electro-optic sampling technique, a 1 mm thick (110) ZnTe nonlinear crystal, was used for the detection of the THz pulses. The experimental setup can measure the loss and dispersion properties of materials up to 1.0 THz range.

3. Results and discussion

3.1. BiZN ceramic materials

When the BiZN ceramics prepared by the one-step process were sintered directly, the $Bi_5Nb_3O_{15}$ phase was preferentially resulted (Fig. 1a–c). The $Bi_5Nb_3O_{15}$ phase can be completely eliminated only by sintering the materials at high enough temperature, i.e. 1100°C (4 h). Secondary phase, presumably ZnO-deficit $BiNbO_4$, is induced for the materials sintered at 1200°C (4 h), which is ascribed to the ZnO vaporization loss. The materials contain only $Bi_2ZnNb_2O_9$ (cubic BiZN) and $Zn_3Nb_2O_8$ phases when properly sintered. The characteristics of the materials are optimized for 1100°C (4 h) sintered samples (Fig. 2a–c), which possess high density (~7.0 g/cm^3), large dielectric constant ($K \cong 67$), high quality factor ($Q \times f \cong 80{,}000$ GHz) and small temperature coefficient of resonance frequency ($\tau_f \cong -10$ ppm/°C).

When the BiZN composite materials were prepared by a two-step mixed oxide route (Fig. 1d–f), the sintered materials contain perovskite $Bi_2ZnNb_2O_9$ (*c*-BiZN) phase, and a small proportion of $Zn_3Nb_2O_8$ when sintered at 1000–1050°C (Fig. 1e and f). Sintering at too high temperature also induced the formation of secondary phase, which is, again, presumed to be the ZnO-deficit $BiNbO_4$ phase resulted from ZnO vaporization loss.

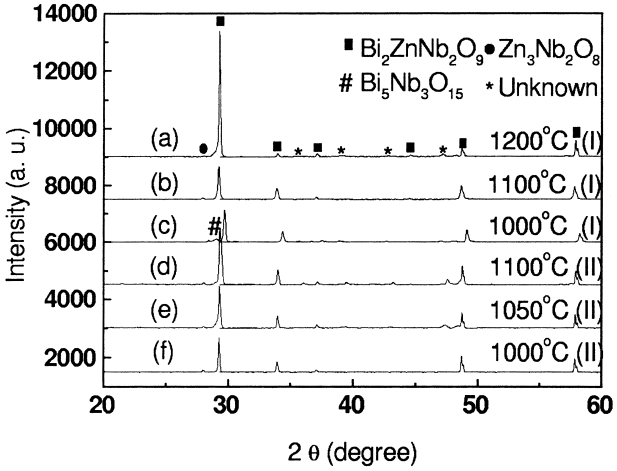

Fig. 1. X-ray diffraction patterns of BiZN + ZN materials one-step sintered at (a) 1200°C, (b) 1100°C, and (c) 1000°C for 4 h (labeled as I) and two-step sintered at (d) 1100°C, (e) 1050°C, and (f) 1000°C for 4 h (labeled as II).

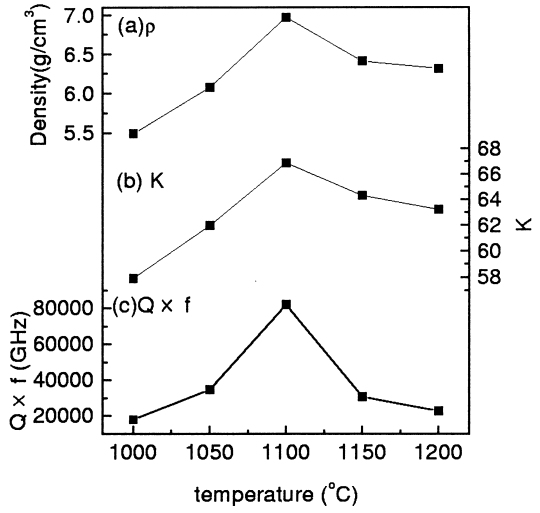

Fig. 2. (a) Density, (b) *K* value, and (c) $Q \times f$ of BiZN + ZN materials one-step sintered at 1000–1200°C for 4 h.

Fig. 3a and b shows that the 1050°C-sintered materials possess highest density (7.2 g/cm^3) and largest dielectric constant ($K = 67$). Fig. 3c and d reveals that the quality factor $Q \times f$ decreases, while the τ_f value increases monotonously, with the sintering temperature. The advantage of 2-step process over the simplified one-step one is that the material's characteristics for the 2-step processed samples are relatively insensitive to the sintering parameters, as compared with those for the single-step processed ones. Furthermore, the above described results imply that the existence of small proportion of ZnO-deficit phase, which is of low $Q \times f$ and

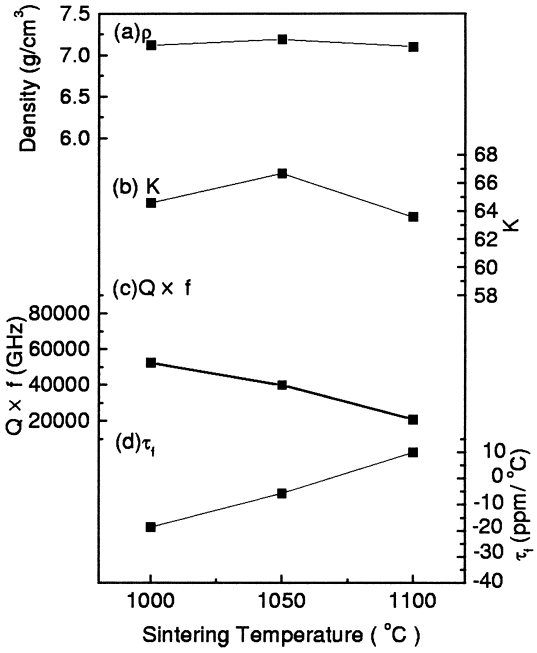

Fig. 3. (a) Density, (b) K value, (c) $Q \times f$, and (d) τ_f of BiZN + ZN materials two-step sintered at 1000–1100°C for 4 h.

high τ_f value, significantly altered the microwave dielectric response of the BiZN–ZN composite materials, even though it does not pronouncedly influence the density and microstructure of the samples.

3.2. BiZN thin films

$Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ (BiZN) thin films were prepared by pulsed laser deposition process. The pulsed laser deposited films are readily crystallized for a substrate temperature higher than 450°C (not shown). Secondary phase appears for the films grown at a substrate temperature higher than 550°C, which is presumably induced by Zn-loss phenomenon. To compare the dielectric response of the BiZN thin films with that of the bulk materials in the same frequency region, terahertz transmission spectroscopy (TTS) is utilized. Typical time domain terahertz (THz) waveforms through the free space and those with BiZN ceramic samples inserted in optical path are illustrated in Fig. 4. After Fourier transformation, the complex transmission function $t(\omega)$ in frequency response of the materials can be computed from the ratio of electric field E for the terahertz (THz) waveforms, before and after passing through the samples, i.e.

$$t(\omega) = \frac{E(\omega)_{\text{samples}}}{E(\omega)_{\text{empty}}} \frac{4N \exp[i\omega(N-1)d/c]}{(N+1)^2} \times \sum_{a=0}^{m} \left[\left(\frac{N-1}{N+1} \right) \exp(i\omega Nd/c) \right]^{2a} \quad (1)$$

where $N = n + ik$ is the complex optical parameter of the materials, $\kappa = 4\pi k/\lambda$ is the absorption coefficient of the materials, $2m$ is the number of internal reflections in the samples, c is the light speed in free space and d is the thickness of the samples. Solving the Eq. (1) by numerical method, the dielectric response of the material, can then be calculated using the relationship,

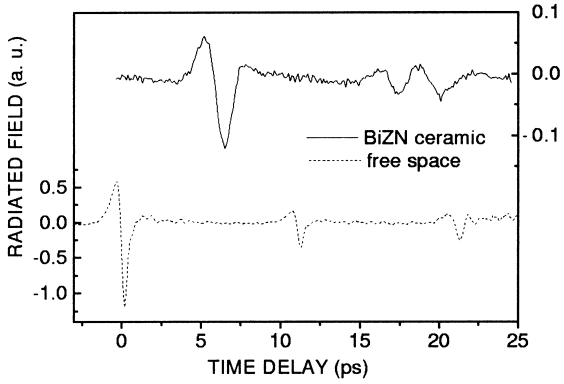

Fig. 4. Typical time domain THz waveforms through the free space and with the BiZN ceramics inserted in the optical path.

$$\varepsilon' = n^2 - k^2 \quad (2)$$

$$\varepsilon'' = 2nk \quad (3)$$

The dielectric constant (ε') thus obtained is $(\varepsilon')_{\text{b·THz}} = 69$ at around 0.5 THz, which is close to the K value for ceramics at microwave frequency. The quality factor, which is around $(Q \times f)_{\text{b·THz}} = 4600$ GHz, is about one order of magnitude smaller than the $Q \times f$ value at 10 GHz.

Similarly, the time-domain TTS for the BiZN/MgO thin films can be converted into frequency domain after Fourier transformation, and the dielectric properties of the BiZN thin films can be evaluated. The results show that the dielectric constant (ε') of the BiZN thin films, $(\varepsilon')_{\text{f·THz}} \cong 32-40$ is markedly smaller than the ε' value of BiZN bulk materials. Moreover, the quality factor calculated for the BiZN thin films is $(Q \times f)_{\text{f·THz}} \cong 1.02$ THz = 1020 GHz at 0.8 THz, which is again pronouncedly smaller than that of bulk material.

4. Conclusions

BiZN bulk ceramic materials were prepared by mixed oxide process and BiZN thin films were prepared by pulsed laser deposition (PLD) process. The bulk materials can achieve high density (7.2 g/cm^3), large dielectric constant ($K = 67$), high quality factor ($Q \times f \cong 80,000$ GHz) and small temperature coefficient of resonance frequency ($\tau_f \cong -6$ ppm/°C). Direct measurement on the dielectric response of BiZN ceramic materials and thin films using THz spectroscopy indicates that in THz frequency region, the dielectric constant and quality factor for the BiZN thin films are pronouncedly smaller than those for the bulk materials.

Acknowledgements

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