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Correlation of microwave dielectric properties and crystallinity for pulsed laser deposited $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ thin films

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Abstract

Correlation of microwave dielectric properties of $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$, BiZN thin films, which were pulsed laser deposited on Si(100) substrates, with crystallinity of BiZN phase was examined using Fourier Transform Infrared (FTIR) spectroscopy. Rigid-ion model analysis from FTIR spectra of the films reveals that the magnitude of effective charge for oxygen increases with improved crystallinity for BiZN films. In contrast, lattice vibrational modes of the films, which occur at $\omega_{01} = 341$ cm^{-1}, $\omega_{02} = 522$ cm^{-1}, and $\omega_{03} = 612$ cm^{-1}, insignificantly change with films' crystallinity. It implies that better crystallinity will induce higher polarization in BO_6 oxygen octahedral, which improves microwave properties of pyrochlore materials. The dielectric constant measured at 200 cm^{-1} increases with substrate temperature used for depositing BiZN films, inferring that dielectric properties in low frequency regime of far infrared region are predominantly contributed by ionic polarization, and are strongly related to effective charges of oxygen species.

Keywords: Dielectric properties; Effective charge; FTIR; Microwave dielectric thin films; Pulsed laser deposition

1. Introduction

Recent investigations about the microwave dielectrics indicate that Bi_2O_3–ZnO–Nb_2O_5 series materials[1–5] exhibit marvelous properties such as high dielectric constant, low dielectric loss, adjustable temperature coefficient of resonance frequency and lower temperature necessary for sintering. The same marvelous microwave dielectric properties of the films are also expected, but dielectric properties of thin films inferior to those of bulk materials are usually observed in experiments. For expanding the applications of the materials, dielectric mechanism of thin films are strongly concerned. However, direct measurements of dielectric properties of thin films usually involve metallic conduction and stray field losses, and are hard to be actually performed. Fourier Transform Infrared (FTIR) spectroscopy has become a powerful tool[6] for estimating the dielectric properties of materials in the microwave frequency region and is thus adopted to study the microwave dielectric mechanism of BiZN thin films.

Effective ionic charges have been studied as the parameters related to dielectric properties.[7–9] In this article, we obtain the effective charges of oxygen ions of the films deposited at different temperatures from fitting the FTIR spectrum, and the related dielectric mechanism of the films are discussed.

2. Experimental procedure

$Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$, BiZN, target materials were prepared by conventional mixed-oxide process including mixing, calcining, pulverizing, pelletizing and sintering steps. The BiZN thin films were prepared by pulsed laser deposition (PLD) technique, 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}. Si(100) substrates were used for growing the thin films.

The phase constituents were examined using X-ray diffractometer (Rigaku, Dmax/IIB). In FTIR spectro-

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scopy, transmittance was measured over far infrared region (200–1200 cm^{-1}) using a spectrometer, PERKIN-ELMER System 2000, which possesses a resolution of 4 cm^{-1}. The transmittance spectra of BiZN films were analyzed using the Lorentz model[10] to obtain the dielectric properties of the films.

3. Results and discussion

Fig. 1 reveals that the $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$, BiZN thin films deposited on Si(100) substrates are readily crystallized, forming pyrochlore BiZN phase, for a substrate temperature higher than 450 °C. The crystallinity of BiZN thin films increases with deposition temperature markedly. The films are (222) preferentially oriented and the proportion of grains oriented in (222) direction, estimated from the integral intensity of diffraction peaks in XRD patterns, is about 73%, for BiZN films synthesized at 600 °C. The films deposited at 400 °C or lower substrate temperature are of amorphous structure (not shown).

The real part (ϵ_1) and the imaginary part (ϵ_2) of dielectric constant in optical frequency regime were evaluated from the transmission maxima (T_{max}) and minima (T_{min}) of the optical transmission spectra (OTS) for BiZN/MgO thin films. Optical variation of ϵ_1 and ϵ_2 with wavelength thus obtained for BiZN/MgO films are shown in Fig. 2(a) and (b), respectively, indicating that the ϵ_1 and ϵ_2 values are essentially independent of wavelength in optical regime ($\lambda = 450$–700 nm or $1/\lambda = 1.43\times10^4$–$2.22\times10^4$ cm^{-1}).

The dielectric properties of the films can be derived from the FTIR transmission spectra using the Lorentz model. According to the dispersion theory,[10] ϵ_1 and ϵ_2 as functions of frequency are given by:

$$\varepsilon_1 = \varepsilon_\infty + \sum_i \frac{\Omega_i^2(\omega_{0i}^2 - \omega^2)}{(\omega_{0i}^2 - \omega^2)^2 + \gamma_i^2\omega^2} \quad (1a)$$

$$\varepsilon_2 = \sum_i \frac{\Omega_i^2\gamma_i\omega}{(\omega_{0i}^2 - \omega^2)^2 + \gamma_i^2\omega^2} \quad (1b)$$

where ω_{oi} is the resonance frequency, γ_i is the damping coefficient, Ω_i is the resonance strength, ϵ_∞ is the dielectric constant caused by the electronic polarization at high frequencies. The real part (ϵ_1) and imaginary part (ϵ_2) of dielectric constant for these BiZN films analyzed in far infrared frequency region, 200 to 700 cm^{-1}, are shown in Fig. 3. Fig. 3(a) indicates that the real parts of dielectric constants (ϵ_1) are around 13–18 in low wavenumber regime, i.e., in microwave frequency range, increase slowly with wavenumber up to 280 cm^{-1} and drop abruptly at around $\omega_{01} = 341$ cm^{-1}. The drop in ϵ_1 value corresponds to polarization resonance associated with lattice vibration, which is clearly demonstrated in dispersion of ϵ_2 value [Fig. 3(b)]. These figures also indicate the existence of two other lattice vibrational resonances at around $\omega_{02} = 522$ cm^{-1}, and $\omega_{03} = 612$ cm^{-1}.

Fig. 3(a) indicates that the real part of dielectric constant at lower frequency end (200 cm^{-1}) of far infrared regime changes pronouncedly, whereas that at higher frequency end (700 cm^{-1}) varies insignificantly with substrate temperature. The ϵ_1 value at 200 cm^{-1} is small for 450 °C-deposited films ($\epsilon_1 \approx 13$). It increases as the crystallinity of the films improves with substrate

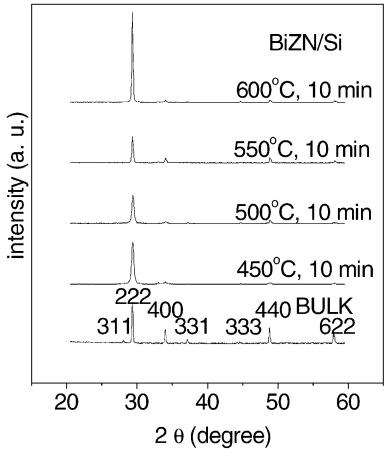

Fig. 1. X-ray diffraction patterns of BiZN films deposited on Si at 450–600 °C for 10 min.

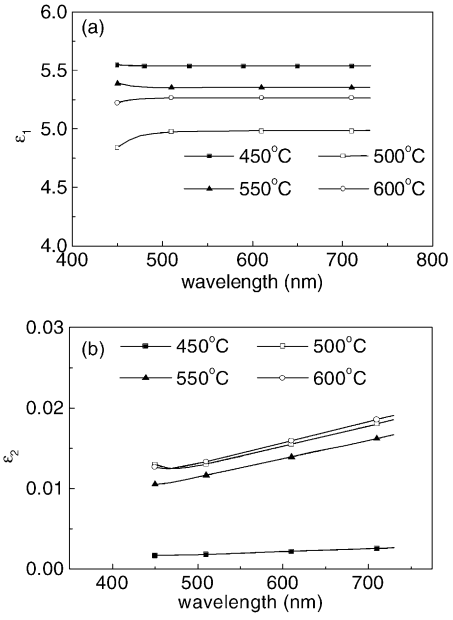

Fig. 2. (a) Real parts, and (b) imaginary parts of the dielectric constants analyzed by optical transmission spectroscopy (OTS) for BiZN thin films deposited on MgO.

temperature, reaching the highest value for 600 °C-deposited films ($\epsilon_1 \approx 18$). Moreover, Fig. 3(a) indicates that the real part of dielectric constant extrapolated from FTIR spectrum to higher frequency region, $\epsilon_1 \cong 6$, is essentially the same as ϵ_1 value estimated from OTS, optical $\epsilon_1 \cong 4.7$–5.5 [Fig. 2(a)] The implication of these results is that there is no lattice vibrational resonance contributing to the polarization process for BiZN materials between the far infrared and optical frequency regions. These results infer that the dielectric response in high frequency regime (700 cm^{-1}) is mainly contributed by electronic polarization process, which is less affected by crystalline quality. In contrast, the dielectric responses for the materials in the low frequency regime (200 cm^{-1}) are mainly predominated by the lattice vibrational resonances, which are strongly influenced by crystalline quality. Fig. 3(b) shows that the deposition temperature does not markedly alter the lattice vibrational modes of the materials appearing in the imaginary part of dielectric constant, ϵ_2.

To understand the factor which alters the dielectric properties of the BiZN thin films deposited at different substrate temperatures, the longitudinal optical (LO) and transverse optical (TO) phonons were analyzed from optical conductivity and loss function derived from FTIR spectra, which are shown in Fig. 4. The frequencies of TO and LO oscillations can be obtained directly from the peak positions of optical conductivity and loss function respectively, as shown in Fig. 4. The TO frequencies are related to the strongest absorption, whereas the LO frequencies involve long-range changes in the dipole moments along the direction of propagation which cause losses. $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ materials can be described by pyrochlore structure with a formula $A_2B_2O_7$ and space group Fd3m. The larger A cation resides in eightfold coordination while the smaller B cation resides in sixfold coordination, forming a BO_6 oxygen octahedral. The vibration modes of pyrochlores at about 341, 522, and 612 cm^{-1} are presumably associated with A–O bonds, B–O bond bending, and B–O bond stretching, respectively.

Table 1 shows the TO, LO frequencies of three different vibration modes. It should be noted that the frequencies ω_{TO1}, ω_{LO1} are insensitive to deposition temperatures, whereas the LO–TO splitting of vibration modes at about 522 cm^{-1} (ω_{TO2}), and 612 cm^{-1} (ω_{TO3}) varies significantly with deposition temperatures. This result implies that BO_6 oxygen octahedral plays an important role in the mechanism for the dielectric properties of the BiZN thin films. The better crystal structure will improve the polarizability of BO_6 oxygen octahedral and thus increases microwave dielectric properties for BiZN thin films.

The magnitude of the effective charge can be evaluated from the equations of motion of ions for longitudinal (LO) and transverse (TO) directions and the condition

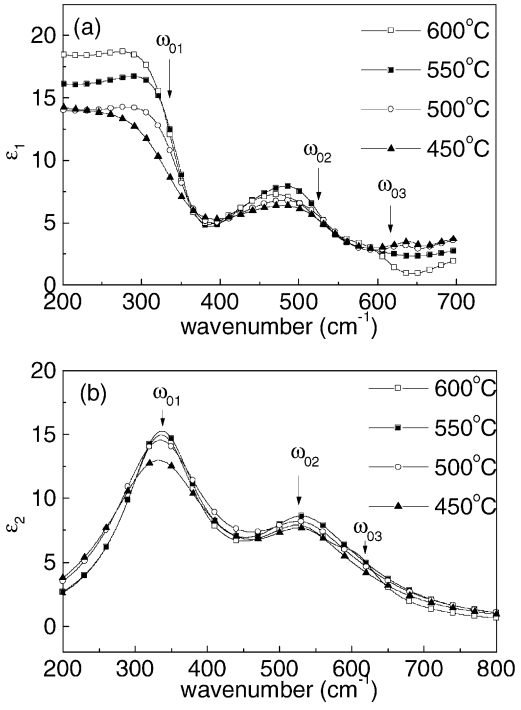

Fig. 3. (a) Real parts and (b) imaginary parts of dielectric constants calculated from far infrared spectra of BiZN thin films deposited on Si at 450–600 °C.

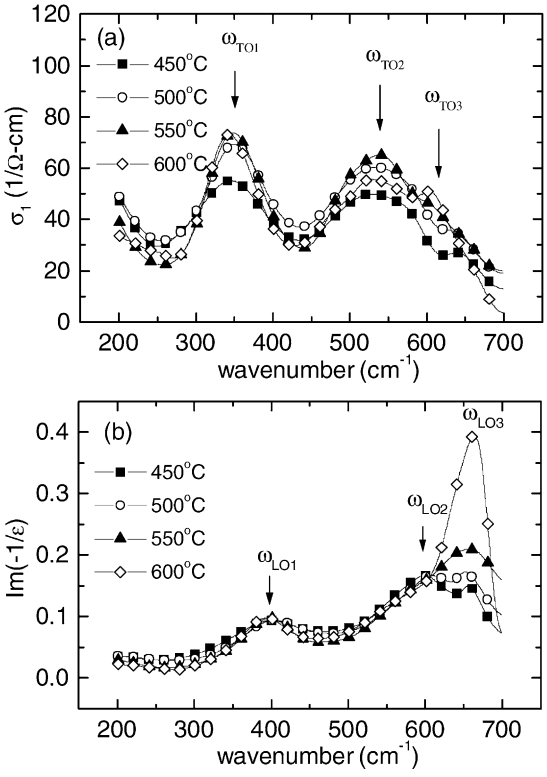

Fig. 4. (a) Conductivity and (b) loss function obtained from Lorentz-model fit to the transmittance of BiZN/Si thin films deposited at 400–600 °C.

Table 1
The TO, LO frequencies and oxygen effective charge of BiZN/Si thin films deposited at 400–600 °C

Deposition temperature	ω_{TO1} (cm^{-1})	ω_{LO1} (cm^{-1})	ω_{TO2} (cm^{-1})	ω_{LO2} (cm^{-1})	ω_{TO3} (cm^{-1})	ω_{LO3} (cm^{-1})	Effective Charge (e)
450 °C	338	400	538	599	649	656	0.738
500 °C	347	404	540	600	643	652	0.780
550 °C	347	398	525	585	609	657	0.982
600 °C	342	394	523	579	613	664	0.986

of charge neutrality in the crystal, i.e., the effective charge of ions based on a rigid-ion model can be estimated from TO–LO splitting by using Scott[11] model:

$$\sum_i \left[\omega_{LOi}^2 - \omega_{TOi}^2\right] = \frac{4\pi}{V}\sum_j \frac{(Z_j e)^2}{m_j} \quad (2)$$

where i is the sum over all LO–TO splitting, V is the volume of the unit cell and j is the sum over all ions with mass m_j and effective charge Z_j in unit cell. Combining with the equation from charge neutrality:

$$\sum_j Z_j = 0, \quad (3)$$

we can solve Z_j only when the number of unknown Z_j is equal two, because only two different equations are available, which can be solved for two unknowns. In the case of $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ materials, the contribution of oxygen ions in Eq. (2) will dominate the j summation, since oxygen is much lighter than other atoms. Thus by neglecting all but oxygen contributions in Eq. (2), we can approximate the value of the effective charge for oxygen ion as shown in Table 1. The results imply that the effective charge for oxygen increases with improving the crystallinity of the films.

4. Conclusion

The $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$, BiZN thin films were pulsed laser deposited on Si(100) substrates, and the crystalline BiZN phase can be obtained for a substrate temperature higher than 450 °C. FTIR measurements reveal the presence of lattice vibrational modes of the films at about $\omega_{01} = 341$ cm^{-1}, $\omega_{02} = 522$ cm^{-1}, and $\omega_{03} = 612$ cm^{-1}. Real part of dielectric constant extrapolated to microwave frequency is about 13–18 and approaches a constant value ($\epsilon_1 \cong 6$) in optical high frequency regime ($1/\lambda > 10^4$ cm^{-1}), which corresponds to the ϵ_1 value measured in OTS. The dielectric properties at low frequencies are presumably contributed by ionic polarization in far infrared region, and are strongly related to the effective charge of oxygen. Rigid-ion model analysis implies that better crystallinity will cause higher polarization in BO_6 oxygen octahedral, which significantly affects microwave dielectric properties of the pyrochlore BiZN thin films.

Acknowledgements

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