CHARACTERIZATION OF $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ AND $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$ MICROWAVE DIELECTRICS IN OPTICAL AND MICROWAVE FREQUENCY REGIONS

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$\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$, BMT, and $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$, BiZN, thin films were grown on [100] MgO single crystal substrates using pulsed laser deposition process. The high-frequency dielectric properties of thus obtained thin films were measured using optical transmission spectroscopy. Characteristics of BMT thin films were compared with those of BiZN thin films. BMT films need higher substrate temperature ($\sim 800^\circ$) and longer deposition time (~ 75 min) than those of BiZN thin films for getting better crystallinity. The index of refraction n and the absorption coefficient κ of these films derived from their optical transmission spectra reveal that both optical parameters (n , κ) for the BMT films are smaller than those of BiZN films. These behaviors are intimately correlated with lower microwave dielectric constant K and higher quality factor $Q \times f$ characteristics for BMT bulk materials, as compared with those of BiZN bulk materials.

1 Introduction

Microwave dielectric thin films have remarkable advantages in (1) lower operation voltage, (2) faster response, (3) feasible in epitaxial growth and most of all, (4) nonlinear relationship in dielectric properties [1-2], which increases the tunability. Especially, $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$, BMT, and $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$, BiZN, microwave dielectrics exhibit marvellous properties such as high dielectric constant, low dielectric loss, adjustable temperature coefficient of resonance frequency, and low firing temperature necessary for sintering. The same marvellous microwave dielectric properties are expected in a thin film form. Pulsed laser deposition (PLD) technique [3] is adopted in this article for synthesizing BMT and BiZN microwave dielectric thin films. Highly textured thin films were obtained and their optical parameters were derived from the corresponding optical transmission spectra. Both the synthesizing parameters and optical properties of the BMT and BiZN films were observed to correlate with the bulk materials intimately.

2 Experimental procedure

$\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$, BMT, and $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$, BiZN, target materials were prepared by conventional mixed-oxide process. MgO [100] substrates were used for growing the thin films. 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 $400^\circ\text{--}600^\circ$ in 0.1 mbar oxygen pressure (P_{O_2}) for 30 min, followed by 10 min of *in-situ* annealing at the depositing temperature under 1 atm P_{O_2} . The BMT thin films were prepared by a 2-step PLD process using a KrF excimer laser ($\lambda=248$ nm, Lambda Physik) with

an energy density of 7 J/cm^2 . The films were first deposited at 200°C in $0.08 \text{ mbar } \text{Po}_2$ for 75 min, followed by post-annealing at 850°C in air for 60 min. It should be noted that 2-step PLD process is utilized for synthesizing the BMT films, simply because of the high substrate temperature (850°C) required for crystallization of the materials is too difficult to maintain in the *in-situ* deposition process.

3 Results and discussion

The crystalline phases of the films were determined using X-ray diffractometer (Rigaku, Dmax/IIB) with $\text{Cu K}\alpha$ radiation. The high-frequency properties of the films were investigated using optical transmission spectroscopy (Hitachi U-3410).

The crystal phase of the $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$, BMT thin films deposited on $\text{MgO}[100]$ substrates, which is a perovskite structure, varies with post-annealing temperature significantly. The as-deposited films are amorphous, which start to crystallize for an annealing temperature higher than 800°C . The films are $[200]$ preferentially oriented when post-annealing at 850°C for 60 min (Fig. 1(a)).

Fig. 1 X-ray diffraction patterns of (a) BMT/MgO thin films deposited at 200°C for 75 min, followed by post-annealing at 850°C for 60 min, (b) BiZN/MgO thin films *in-situ* deposited at 500°C for 30 min.

Figure 2(a) shows the optical transmission spectra of the BMT/MgO thin films. The optical parameters, including refractive index (n) and absorption coefficient (κ), can be derived from the maximum transmittance (T_{max}) and minimum transmittance (T_{min}) [4].

The average optical refractive index (n) of the films is around $n=2.10$ and the absorption coefficient (κ) of the BMT/MgO films is around $\kappa=3.18 \times 10^{-4} \text{ nm}^{-1}$ in the region of $\lambda=320\text{--}780 \text{ nm}$, which are insensitive to post-annealing temperature and deposition time (not shown). The thickness of the films can also be estimated [4] and is approximated as $(d)_{\text{BMT}} \approx 257.2 \text{ nm}$. It should be noted that the dispersion of n and κ in the short wavelength regime were truncated due to the inaccuracy induced by large absorption in this region, which is arbitrarily chosen as the λ corresponding to $T_\lambda=0.8 T_{max}$. Knowing the absorption coefficient (κ) at each wavelength (λ), the energy gap (E_g) of the BMT films can also be estimated from the optical transmission spectra, using quantum theory of solids [4]. The results of calculations reveal that $(E_g)_{\text{BMT}}=3.702 \text{ eV}$ for BMT thin films.

The crystalline phase of $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$, BiZN, films can be formed on MgO substrates much more easily, as compared with that of BMT films. However, the crystalline phase of the BiZN/MgO, which is a pyrochlore structure, also varies markedly with the deposition temperature. The crystalline BiZN films can be obtained at 450°C substrate temperature. The films are $[222]$ predominated when deposited at 500°C and are randomly oriented when deposited

at temperature higher than 550°. No secondary phase is induced even at 600° substrate temperature. All the BiZN/MgO films exhibit similar crystal structure, [222] predominated, regardless of the film thickness, which is illustrated by typical X-ray diffraction patterns in Fig. 1(b).

Fig. 2 Optical transmission spectra of (a)BMT/MgO thin films deposited at 200° for 75 min, followed by post-annealing at 850° for 60 min, (thickness $(d)_{\text{BMT}} \approx 257.2$ nm) and (b)BiZN/MgO thin films *in-situ* deposited at 500° for 30 min (thickness $(d)_{\text{BiZN}} \approx 289.3$ nm).

The optical transmission spectra of the BiZN/MgO thin films is shown in Fig. 2(b) and the optical parameters, including refractive index (n) and absorption coefficient (κ), are derived from the maximum transmittance (T_{max}) and minimum transmittance (T_{min}) [4]. These evaluations reveal that the average optical refractive index (n) of the films is around $n=2.37$, which is much larger than the n value of BMT films, and the absorption coefficient (κ) of the films is around $\kappa \approx 3.88 \times 10^{-4} \text{ nm}^{-1}$, which is about the same value as that of BMT films, in the $\lambda=320\text{--}780$ nm region. The n and κ of BiZN films are also insensitive to substrate temperature and deposition time. The thickness of the BiZN films is estimated to be around $(d)_{\text{BiZN}} \approx 289.3$ nm, which is very close to that of BMT films. The energy gap (E_g) of the BiZN films, which is, again, estimated from the optical transmission spectra ($(E_g)_{\text{BiZN}} = 3.171$ eV), is smaller than the E_g value of BMT films.

It is interesting to notice that the optimized thin film deposition temperature correlates very well with the sintering temperature necessary for obtaining bulk ceramics. BMT materials need very high sintering temperature (1650°) and long soaking time (8 h) to fully densify the bulk ceramics for optimizing the microwave dielectric properties, whereas the BiZN materials need only 1100°×4 h to sinter, shown as footnotes in Table 1. Therefore, it requires very high annealing temperature (~850°) to fully crystallize the BMT films and very long deposition time (~75 min) to reach a thickness almost the same as BiZN films, which were deposited at 500° for 30 min.

	Dielectric constant K^a	$Q \times f$ value ^b	Index of refraction n^b	Optical dielectric constant ϵ_{op}^b	Absorption coefficient $\kappa (\text{nm}^{-1})^b$
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^a Microwave properties were measured at 6 GHz.

^b Optical properties were measured at $\lambda=500$ nm.

BMT ^c	21	600,000	2.098	4.40	3.18×10^{-4}
BiZN ^d	67	82,000	2.365	5.59	3.88×10^{-4}

Table 1 Comparison on microwave characteristics of BMT and BiZN materials with their optical parameters.

The difference in optical parameters for BMT and BiZN films correlates intimately with their bulk properties. The BMT materials possess smaller dielectric constant ($(K)_{\text{BMT}} \approx 21$) and better quality factor ($(Q \times f)_{\text{BMT}} \approx 600,000$) at 6 GHz operating frequency, as compared with those of BiZN materials, which are $(K)_{\text{BiZN}} \approx 67$ and $(Q \times f)_{\text{BiZN}} \approx 82,000$. The dielectric constants at optical frequency ($f = 6 \times 10^5$ GHz or $\lambda = 500$ nm) of these materials can be estimated using the relationship, $\epsilon_{op} = n^2$, which are listed in Table 1, showing that the higher the microwave dielectric constant (K) for the ceramics, the larger the refractive index (n) and optical dielectric constant (ϵ_{op}) for the thin films. The absorption coefficient (κ) is smaller for BMT materials, since the Q-factor of these materials is much larger. However, the correlation between K value and Q-factor for these materials is not as close as that between the index of refraction (n) and microwave dielectric constant (K). The cause of discrepancy is probably the presence of abundant defects in the thin films, which degrade the quality of the materials.

The dielectric constant of the materials (ϵ_{op}) estimated from their optical refractive index is markedly smaller than the dielectric constant measured at microwave regime (K). Such a phenomenon is presumably due to the fact that ionization polarization operating at microwave regime is inactive at optical regime. However, direct measurement on thin films' microwave dielectric properties is necessary in order to investigate the frequency dependence of the dielectric behavior for the thin films. Microstrip line devices fabricated on these films were proposed and Terahertz spectroscopy was adopted for the evaluation of dielectric properties in microwave and higher frequency regimes, respectively. The results of these measurement will be repeated in the near future.

In summary, high quality BMT and BiZN thin films were synthesized on MgO substrates using pulsed laser deposition process. The optical parameters of these films were evaluated from their optical transmission spectra. The optimized deposition parameters for synthesizing thin films correlate closely with the sintering conditions necessary for densifying the corresponding ceramic materials, whereas the optical parameters of these films correlated intimately with the microwave dielectric properties of the corresponding bulk materials.

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^c Ba(Mg_{1/3}Ta_{2/3})O₃ (BMT): the target materials were sintered at 1650° for 8 h and the films were deposited at 200° for 75 min, followed by post-annealing at 850° for 60 min.

^d Bi₂(Zn_{1/3}Nb_{2/3})₂O₇ (BiZN): the target materials were sintered at 1100° for 4 h and the films were deposited at 500° for 30 min.

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