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Fabrication of bismuth titanate ($Bi_4Ti_3O_{12}$) thin films: Effect of annealing temperature on their structural and optical properties

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Abstract. Bismuth titanate ($Bi_4Ti_3O_{12}$) ceramics, so-called BiT, have many modern applications in microelectronics, sensors, and capacitors. In this study, the related solutions for fabricating BiT thin films were prepared and, then, coated on glass substrates by using the sol-gel technique and the spin coating instrument. The X-ray diffraction patterns of our samples indicated that the crystalline phases of the BiT were orthorhombic. Based on the transmission-spectra analysis, the samples are transparent in a visible spectrum, and their optical energy gaps were found to be 3.36 eV and 3.41 eV for the BiT thin films annealed at 600°C and 650°C, respectively. Other physical quantities, such as refractive index, thickness, extinction coefficient, and dielectric constant, were estimated by Swanepoel's method. The results show that as the annealing temperature rises, the real part of the dielectric constant becomes larger, that is, our samples are good dielectric materials.

1. Introduction

Ferroelectric oxides have many applications in microelectronics, sensors, and capacitors due to their ferroelectric and optoelectronic properties as well as high dielectric constants [1-3]. Bismuth titanate ($Bi_4Ti_3O_{12}$), so-called BiT, is a lead-free ferroelectric material [4] that was firstly discovered in 1949 by Aurivillius and Feng [5,6]. BiT belongs to a family of materials well known as Aurivillius ferroelectrics or ferroelectrics containing bismuths layers, and it is generally defined by the following chemical formula:

$$A_{m-1}Bi_2B_mO_{3m+3} = (Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}, \quad (1)$$

where A is a cation with +1, +2, or +3 oxidation state having a large ionic radius like Bi^{3+}, Pb^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, and K^+, B is a cation with a small ionic radius like W^{6+}, Ti^{4+}, Nb^{5+}, and Fe^{2+}, and m is an integer number from 1 to 8 or a fractional number such as 2(1/2) and 3(1/2). Bismuth titanate with a formula of $Bi_4Ti_3O_{12}$ corresponds to $B = Ti$, $A = Bi$, and $m = 3$ in Eq. (1). First, Aurivillius et al. [7] predicted a tetragonal or quasi-tetragonal structure for a bismuth oxide layer [6]. Further investigations by other researchers showed that most of the Aurivillius compounds [8] have orthorhombic structures in the ferroelectric phase [9]. BiT has an orthorhombic

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Table 1. The compound used in the fabrication of BiT cell.

Structure name	Chemical formula	Molar mass (gr/mol)	Purity (%)
Titanium isopropoxide	$C_{12}H_{28}O_4Ti$	284.215	99.9
Acetic acid glacial	CH_3COOH	60.05	99.9
2-methoxyethanol	$C_3H_8O_2$	76.09	99.9
Acetylacetone	$C_5H_8O_2$	100.13	–

structure with lattice parameters of $a = 5.450$ Å, $b = 5.4059$ Å, and $c = 32.832$ Å. The angle between these lattice vectors, i.e., α, β, and γ, was measured by Rae et al. [10]. Ceramics made of layered compounds of $(Bi_2O_2)^{2+}$ do not have high piezoelectric properties because of their low polarization. However, their high stability and high Curie temperature (550-650°C) might make them potential candidates for important piezoelectric materials [11]. Three main techniques are presently available to fabricate ferroelectric thin films:

1. Physical vapor deposition (PVD);
2. Chemical vapor deposition (CVD);
3. Sol-gel techniques and spray-on technique [12].

Ferroelectric thin films are used in order to exploit the unique electro-optical, piezoelectric, and pyroelectric properties [13,14]. In this investigation, we have fabricated BiT thin films on the glass substrate with the sol-gel technique [15] and, then, studied their optical and structural properties in detail.

2. Experimental method

In this study, the compounds listed in Table 1 are used to fabricate BiT thin films. In order to provide the initial solution, stoichiometric amounts of bismuth nitrate were dissolved into glacial acetic acid; then, the resulting solution was stirred at 70°C using a magnetic stirrer for one hour in reflux conditions. Following the complete dissolution of the bismuth nitrate into the glacial acetic acid, the initial solution was cooled down to room temperature. The second solution was separately prepared by dissolving the titanium isopropoxide into the 2-methoxyethanol. In this step, a small amount of acetylacetone was added to the solution as a stabilizer. In the next step, the initial and second solutions were mixed and, then, stirred using a magnetic stirrer for two hours in reflux conditions. The obtained final solution is transparent with yellow color. The molar mass of the final solution is 0.2 M. The fabrication of the bismuth titanate solution is schematically shown in Figure 1. Finally, the solgel solution was spin-coated onto the glass substrate using a spin coater at 3000 rpm for 30 s. The substrate was cleaned with acetone and methanol and, then, was rinsed in deionized water. The films were heated at

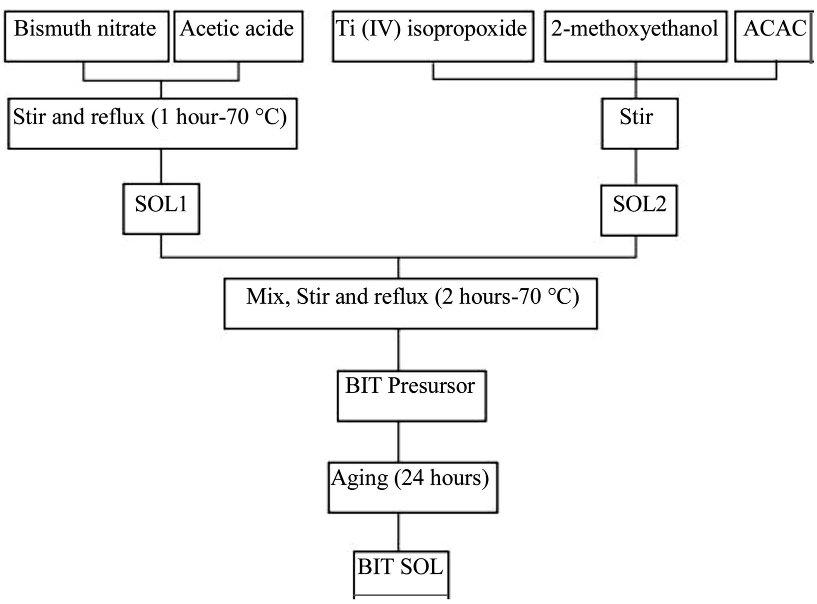

Figure 1. The schematic fabrication processes of BiT sol.

300°C for 10 min on a hot plate to evaporate solvents and organic materials. After repeating this process for ten times, the films were annealed in the temperature range of 600-650°C for one hour in air atmosphere using the same heating rate of 15°C/min. The phase and crystallization of the films were determined by X-ray diffraction patterns (D8-Advance Bruker Cu Kα1; λ= 0.15406 (nm). The surface morphology and microstructure were measured by using a scanning electron microscope (SEM-VP1450). The optical properties of the thin films were also measured by UV-visible 1800 Shimadzu instrument (UV spectrophotometer) [16].

3. Results and discussion

Figure 2 depicts the X-ray diffraction patterns of the BiT thin films deposited on the glass substrates annealed at 550°C, 600°C, and 650°C for one hour in furnace, respectively. The sample annealed at 550°C shows that this temperature is not sufficient to indicate the crystalline phase of $Bi_4Ti_3O_{12}$. The diffraction pattern shows that the crystalline phase of $Bi_4Ti_3O_{12}$ [17] is orthorhombic with lattice constants of $a = 5.44$ Å, $b = 32.81$ Å, and $c = 5.41$ Å. As the temperature rises, the peak intensity (width peak) increases

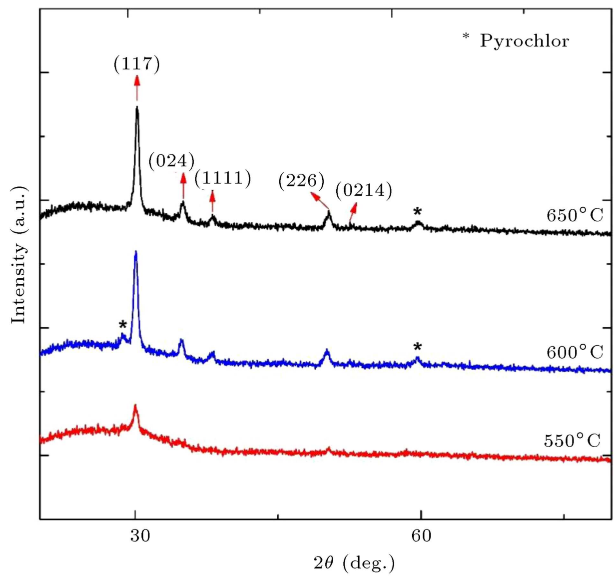

Figure 2. The X-ray diffraction patterns of the BiT thin films deposited on glass substrates annealed at different annealing temperatures for one hour in furnace.

(decreases), which is an indication of an increase in crystallinity of the sample. The peak marked by a star around $2\theta = 28.8°$ in the BiT thin film at 600°C corresponds to the second phase of $Bi_2Ti_2O_7$ [18,19]. According to Figure 2, the percentage of pyrochlorine decreases as the annealing temperature increases to 650°C. According to the Scherrer equation [20] and the main peak of the fabricated phase, one can easily estimate the size of available grains (D) in a thin film as follows:

$$D = 0.9\lambda/\beta\cos(\theta), \tag{2}$$

where λ is the X-ray wavelength, β is the Full Width and Half Maximum (FWHM) peak, and θ is the angle X-ray diffraction. The grains' sizes of the bismuth titanate are shown in Table 2. According to Table 2, the size of the grain has increased with the increasing temperature; however, due to small-sized changes, the size of the nanocrystals is small. However, the size of nanocrystals is sensible for 550°C and 650°C. It is also observed that as the temperature increases, the main peak moves towards larger angles. Hence, as the annealing temperature increases, FWHM decreases; in addition, considering Table 2, it can be observed that bismuth titanate at 650°C has high crystallinity by decreasing the FWHM value. However, for other measurements in this study, we used 600°C and 650°C according to the crystal structures.

Figure 3 shows the SEM images of BiT thin films deposited on a glass substrate annealed at 600°C and 650°C. As is observed in Figure 3, the thin film is a nanostructure with good quality of homogeneity. The grain sizes include $\simeq$ 30 nm and $\simeq$ 40 nm for samples (a) and (b) annealed at 600°C and 650°C, respectively. In order to study the optical properties of BiT thin films, we have used a spectrophotometer to measure the optical transmittance (T) spectra. Figure 4 shows the optical transmittance spectra of the BiT thin film annealed at 600°C and 650°C. According to this figure, many physical quantities regarding the optical properties, such as refractive index (n), absorption coefficient (k), band gap, and dielectric constant, can be achieved [21]. As shown in Figure 4, the high optical transmittance of our BiT thin film with few interference fringes indicates good homogeneity of the prepared sample [22]. As the annealing temperature increases, the transmission coefficient decreases. This

Table 2. Effect of annealing temperatures on structural properties.

Composition	d (hkl)	(2θ) (deg)	FWHM (deg)	Grain size (nm)	Annealing temperature
$Bi_4Ti_3O_{12}$	117	30.056	0.581	14	550
$Bi_4Ti_3O_{12}$	117	30.106	0.502	16	600
$Bi_4Ti_3O_{12}$	117	30.146	0.477	17	650

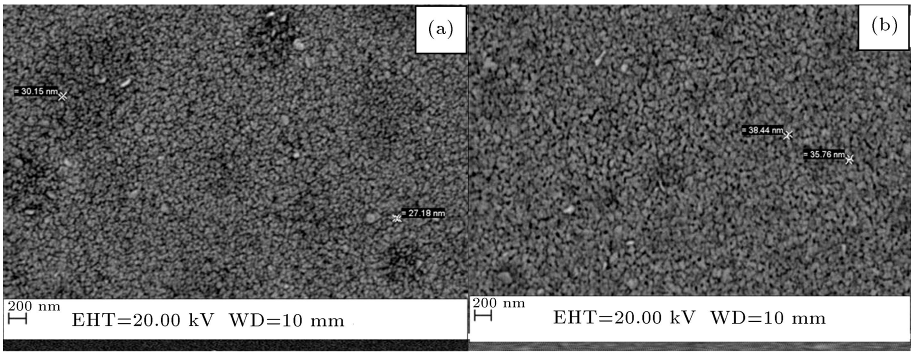

Figure 3. The SEM image of the BiT thin film annealed at (a) 600°C and (b) 650°C.

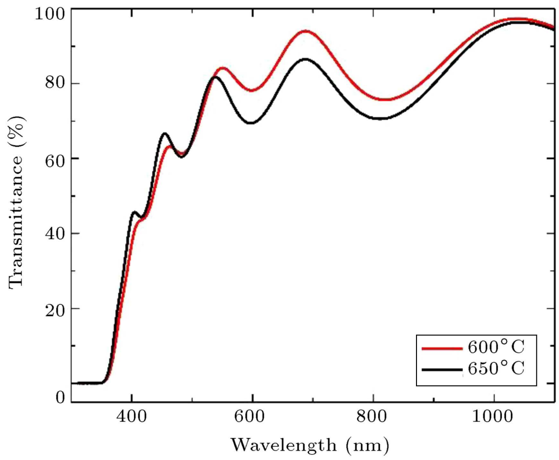

Figure 4. Optical transmittance spectra of the BiT thin film annealed at 600°C and 650°C.

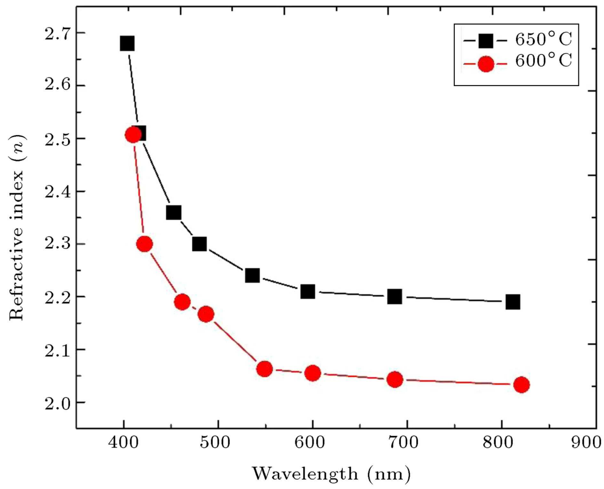

Figure 5. The refractive index (n) dispersion spectra for the BiT thin film annealed at 600°C and 650°C.

can be attributed to an increase in the grain growth and the crystal structure, a decrease in porousness of the layers, and, consequently, an increase in light scattering. Additionally, as the temperature rises, the position of the peaks shifts slightly, indicating a change in the optical band gap. It is also shown that the sample has high transmittance in the visible spectrum about 85%, which is a promising candidate for various photonic and microwave device applications [23]. By using the maximum and minimum of Figure 4, the optical parameters of the sample can also be estimated. In the present study, Swanepoel's method was used to calculate optical parameters such as absorption coefficient (α) and dielectric constant [21]. Based on Swanepoel's method, the refractive index (n) of the BiT thin film in the interference region is estimated as follows:

$$n = [N + (N^2 - s^2)^{1/2}]^{1/2}, \tag{3}$$

where:

$$N = 2n_sT + (n^{2_s} + 1). \tag{4}$$

n_s is the refractive index of the substrate, and

$$T = (T_{\max} - T_{\min})/T_{\max}T_{\min}. \tag{5}$$

Figure 5 shows the refractive index (n) dispersion spectra for the fabricated thin films over the spectral range of 400-800 nm. Generally, as the wavelength increases, the refractive index of the thin film decreases. It is also observed that refractive index (n) increases as the annealing temperature rises [22]. This upward trend corresponds to the condensation and crystallinity of the layers, which is along with the structural packing of the surface. The measured refractive indices (n) of the thin films are in good agreement with the reported experimental results [24]. By using the refractive indices (n_1 and n_2) at two adjacent maximum or minimum:

$$d = \lambda_1\lambda_2/2(\lambda_{1n2} - \lambda_2 n_1), \tag{6}$$

In Eq. (6), the thickness rates of the BiT thin film are estimated to be 508 and 486 nm at 600 and 650°C, respectively. Therefore, d tends to decrease as the temperature rises. In a strong absorption region, the optical energy gap (E_g) can be approximated through the measured optical transmittance (T) spectra using $T = \exp(-\alpha d)$ and the Tauc relation [23-25] $(\alpha h\nu)^{n'} = C(h\nu - E_g)$ where d, α, C, and n' are the thickness of BiT thin film, the adsorption coefficient, a constant,

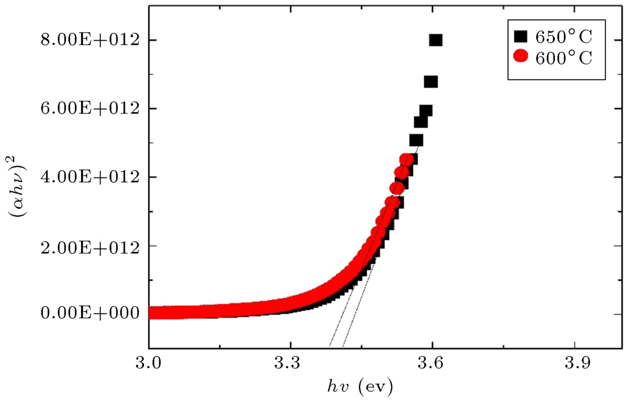

Figure 6. The plots of measured $(\alpha hv)^2$ versus hv of the BiT thin film.

and an exponent representing the transition type in the materials, respectively. Herein, $n' = 2$ represents a direct band gap, while $n' = 1/2$ corresponds to an indirect band gap behavior. Thus, the band gap energy (E_g) can be estimated by extrapolating the liner portion of $(\alpha h\nu)^{n'}$ and $h\nu$ to $(\alpha h\nu)^{n'} \rightarrow 0$. Figure 6 shows the measured $(\alpha h\nu)^2$ versus $h\nu$ (photon energy in eV) of the BiT thin film. Parameter n' is determined to be 2 according to the data in Figure 6, indicating a directly allowed optical transition. It can be seen that E_g value increases from 3.36 eV to 3.42 eV [26,27] as the annealing temperature rises. This can be attributed to an increase in the crystallinity and the grain size. The extinction coefficient (k) can be calculated as follows:

$$k = \alpha\lambda/4\pi. \tag{7}$$

Figure 7 shows the extinction coefficient of the BiT thin films as a function of wavelength (λ). It is observed that k value is very small and increases rapidly at shorter wavelengths, indicating a greater scattering of the photons.

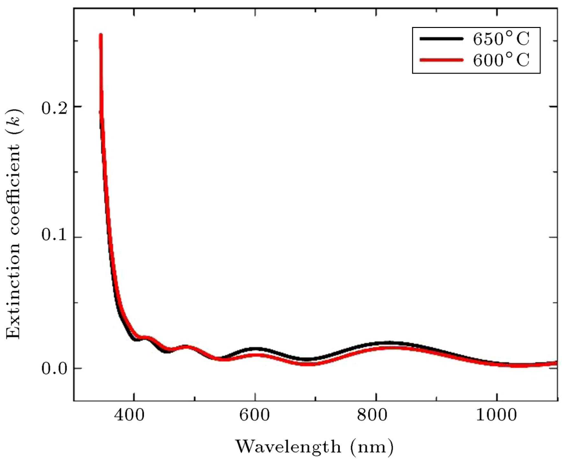

Figure 7. Extinction coefficient versus wavelength for the BiT thin film at 600°C and 650°C.

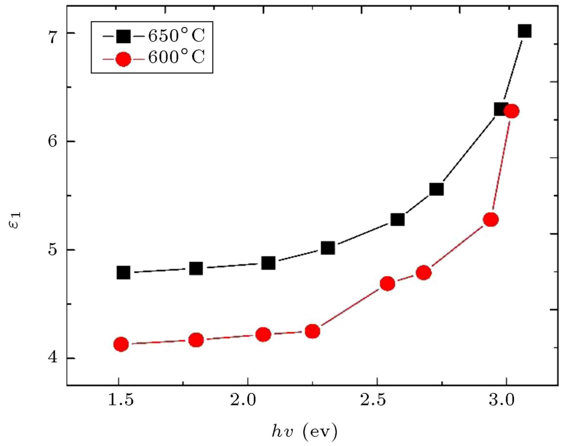

Figure 8. Real part of dielectric constant (ε) versus photon energy for the BiT thin film at 600°C and 650°C.

The real and imaginary parts of the dielectric constants, i.e., Q_1 and Q_2, can be obtained, respectively, as follows:

$$\varepsilon_1 = n^2 - k^2, \tag{8}$$

$$\varepsilon_2 = 2nk, \tag{9}$$

where k and n are the extinction coefficient and the refractive index, respectively. Figure 8 shows the real part of the dielectric constant as a function of photon energy. It is seen that Q_1 has an upward trend as photon energy increases. It is also observed that ε_1 curve is almost linear at long wavelengths. However, this linearity decreases at shorter wavelengths because of a strong interaction between electrons and photons. The real part of the dielectric constant is larger than the imaginary part. It can be also observed that the real part becomes larger by the annealing temperature rise. It indicates that our sample is a good dielectric material [22] (which can be used in electronic applications and sensors [28]).

4. Summary

In summary, bismuth titanate thin films were prepared by the sol-gel technique; then, their optical and structural properties were studied. The X-Ray diffraction pattern shows that the structure of the bismuth titanate thin film is orthorhombic. It was estimated that the size of the grains in the BiT thin film was 16 nm (17 nm) at 600°C (650°C). The SEM images showed that as the annealing temperature increased, the grain size increased and, also, the thin film became a nanostructure with good quality of homogeneity. In the optical transmittance spectra of the thin film at two different temperatures, we observed that our sample was transparent in the visible spectrum. Additionally, the transmittance value decreased when the annealing temperature increased. The optical energy gaps were found to be 3.36 eV and 3.41 eV for our BiT thin films annealed at 600°C and 650°C, respectively. The refractive index (n), thickness of BiT thin films (d), extinction coefficient (k), and dielectric constant (Q_1) were estimated by Swanepoel's method. The refractive index (extinction coefficient) decreased (increases) for longer (shorter) wavelengths. According to our results, as the annealing temperature rises, the real part of the dielectric constant becomes larger, indicating that our sample is a good dielectric material.

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