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# Characterization of optical properties of amorphous $BaTiO_3$ nanothin films

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ABSTRACT

Amorphous barium titanate nanothin films were prepared by sol–gel dip-coating method. According to transmission spectrum, the refractive index and optical band gap of nanothin films have been determined. High transmission spectrum without any fluctuation in visible wavelength region was recorded. Experimental results indicated that the surface morphology of prepared nanothin films were improved and as a result of that, a better optical properties, less optical losses and higher band gap width were obtained in contrast with other reported data. It was found that optical propagation loss of $BaTiO_3$ nanothin film was much lower than normal polycrystalline $BaTiO_3$ thin film. It seems to us that, amorphous barium titanate nanothin films would be suitable for several applications.

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## 1. Introduction

Barium titanate (BT) is one of the most important ceramics due to its outstanding dielectric and ferroelectric properties with different applications such as multilayer capacitors, thermistors and electric devices [1,2]. Thin films of barium titanate with perovskite crystal structure, are known as one of the key materials for use in the solid-state devices, including capacitors, memories, thermistors, sensors and actuators [3,4]. Barium titanate with high transmittance in the visible wavelength region (380–760 nm) is a suitable candidate for various electro-optic applications such as dielectric mirrors. During last decade, there have been many attempts to prepare $BaTiO_3$ thin films [5–8].

Various deposition techniques such as electrochemical deposition [9], sputtering [10], plasma evaporation [11], hydrothermal [12], solvothermal [13] and sol–gel [14–19] have been utilized to prepare $BaTiO_3$ thin films. Sol–gel is currently gaining interest due to low equipment cost and ease of integration with the existing semiconductor technology. Other advantages of the sol–gel method are low-temperature processing, good chemical homogeneity, non-vacuum requirement, easy control of films composition, and uniform deposition on large substrates [19–21]. In addition, the sol–gel technique requires considerably less equipment and is potentially less expensive [22].

In this research; amorphous barium titanate nanothin films on the glass substrate were prepared by sol–gel dip-coating method. Optical properties such as optical spectra, refractive index, and optical band gap of the prepared nanothin film have been evaluated.

## 2. Experimental procedure

In this research, acetate derived barium titanate sol was prepared by using the glacial acetic acid ($CH_3COOH$, Merck, assay 100%), barium acetate ($Ba(CH_3COO)_2$, Merck, assay > 99%), titanium tetraisopropyl alkoxide ($Ti(CH_3CH_3CHO)_4$, Merck, assay > 98%), 2-propanol ($CH_3CH(OH)CH_3$, Merck, assay > 99%) and deionized water as precursors. The chemical compositions of the optimal sols were acetic acid, barium acetate, TTIP, 2-propanol and deionized water with 6:1:1:1:150 M ratio, respectively. Nanothin films were prepared by dipping the substrate (soda-lime glass substrate ($75 \times 25$ mm)) in the sol and withdrawal by the rate of 1 cm/min in ambient atmosphere and temperature. The coated substrates were dried at 100 °C then heat treated at 500 °C with heating rate of 5 °C/min for 1 h in air using an electric oven.

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Optical spectroscopy of barium titanate nanothin films and fourier transform infrared (FT-IR) spectroscopy analyses of sols were performed using UV–visible spectrophotometer Hitachi 3410 and Bruker (Vector 33) instruments, respectively. The TGA analysis and the XRD patterns are provided in order to explain the phase structure and composition of prepared nanothin film. The thermal decomposition characteristics of the dried gel was determined by thermogravimetric analysis (TGA) using a Rhomiric Scientific STA 1500 instrument; the heating rate was 5 °C/min to reach a maximum temperature of 800 °C, with a gas flow rate of 50 ml/min of air. XRD study was performed to get the structure and final phase formation in the system. XRD spectra of the samples have been recorded 2 h in the range 20–80° for crystal phase identification with a Philips PW3710 diffractometer using monochromatized Cu Kα radiation ($k$ = 1.541 Å). The film thickness was measured by using DEK-TAK. The microstructure and surface morphology of the prepared nanothin films were then characterized by using atomic force microscopy (AFM).

## 3. Results

FT-IR analysis is utilized for detection of the existence of the functional groups in the prepared sol and the result is shown in Fig. 1. The characteristic absorption at 3467 $cm^{-1}$ is assigned to the O—H stretching vibration and confirms the existence of water in the sol. Absorption at 3176 $cm^{-1}$ is due to C—H stretching vibration. The peak at 1640 $cm^{-1}$ clearly indicates the existence of acetate groups linked to barium atoms and advocates for the presence of monodentate and bidentate modes in the spectrum caused by barium acetate as it has been reported before [23]. The characterized doublet absorption bands at 1560 $cm^{-1}$ and 1410 $cm^{-1}$ are, respectively, introduced by the asymmetric [$\nu_{as}$(COO−)] and symmetric [$\nu_s$(COO−)] stretching vibrations of carboxylate in the spectrum that assigned to acetic acid [20]. The absorption band at 1040 $cm^{-1}$ can be considered as the alcoholic C—O stretching vibration, and the band at 950, 840, 770, 670, 550 and 480 $cm^{-1}$ are assigned to the characteristic absorption of M—O bonds [20,24]. Sounds like that, the peaks broadening in the range 770–840 $cm^{-1}$ is due to existence of the two formed complexes of Ti and Ba. Two absorption bands at 550 and 670 $cm^{-1}$ are resulted from the Ti–O band and finally, the absorption band at 480 $cm^{-1}$ is representing the Ti–O–Ti band, these are in accordance with previous observations [25,26].

Thermal decomposition of the dried gel as shown by TGA in Fig. 2 reveals the total weight loss of approximately 40%. Three distinct steps of weight loss were observed in the TGA curve. The first weight loss in approximately 50–240 °C is due to the vaporization of residual water and organic solvents. The second one in approximately 240–570 °C is attributed to the pyrolysis of the Ba–Ti organic chelating agent. The third weight loss in approximately 570–770 °C is attributed to the formation of $BaTiO_3$ and the release of $CO_2$ via the reaction between $BaCO_3$ and $TiO_2$. XRD pattern of the prepared thin film and calcined at 500 °C for 1 h is shown in Fig. 3. It is evident from the figure that the prepared thin film is amorphous.

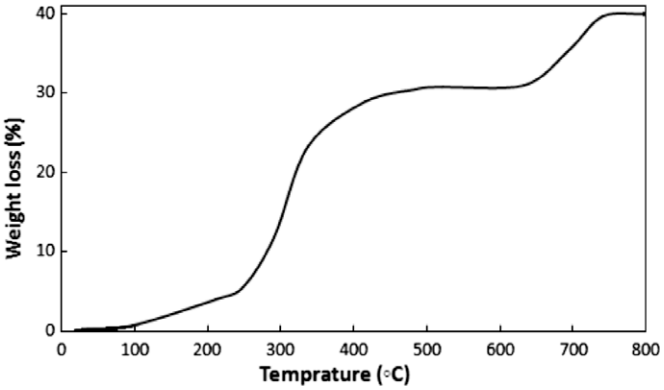


**Fig. 2.** TGA curve for dried gel.

Transmission spectra of the uncoated glass substrate and coated substrate with $BaTiO_3$ nanothin film (~30 nm thickness) were recorded and presented in Fig. 4. In these spectra there are no fluctuations in the transmission spectrum of $BaTiO_3$ nanothin film that, this appealing phenomenon have not been observed in similar researches [4,19,27].

## 4. Discussion

According to Fig. 4, it can be seen that deposited film on the glass was highly transparent in the wavelength range from 400 to 1200 nm with average transmission of 86.5%, which is higher than the previous reported value in similar researches in those, the average value in the range of 70–75% was reported [4,19,27]. It seems to us that the improved optical transmission in this research might be due to optimal ratios selected for sol preparation. As we know, the energy of incident light on the transparent materials is divided in two sections. The first fraction transmits through the material and the other is the losses that are incurred by absorption and reflection [28]. This fact was depicted in Fig. 5. This figure showed the high transparency and consequently low energy losses through reflection and absorption in the visible and near infrared regions. It also indicated the high absorption in the ultra violet region. The transmission of the films was decreased sharply when

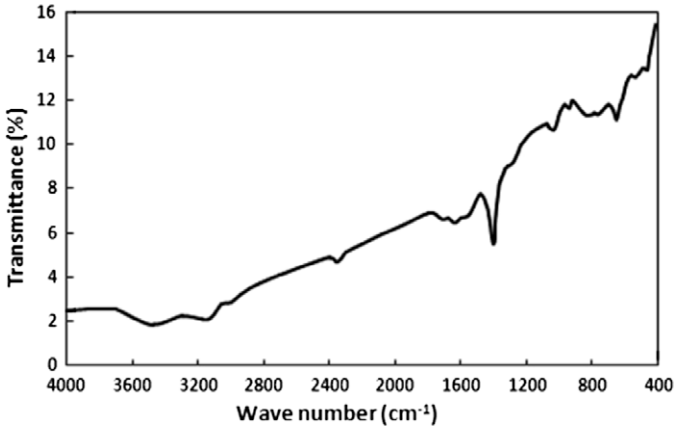


**Fig. 1.** FT-IR spectrum of $BaTiO_3$ sol coated on the glass.

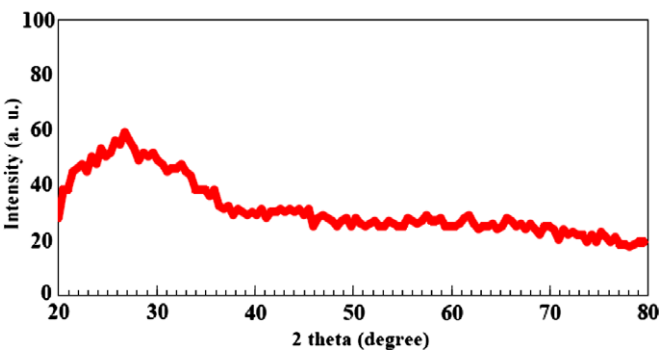


**Fig. 3.** XRD spectra of prepared thin film calcined at 500 °C for 1 h.

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