REVIEW

Highly-transparent Perovskite Thin Films Obtained by a Wet Chemical Processing Method

Rouholah Ashiri*
Materials and Energy Research Center, Dezful Branch, Islamic Azad University, P.O. Box 313, Dezful, Iran

1. Introduction

Barium titanate (BaTiO$_3$; BTO) exhibits high dielectric and ferroelectric responses. It was used for making multilayer ceramic capacitors and for electro-optic applications$^{[1,2]}$. Thin films made by BTO recently have found some applications in industry$^{[3,4]}$. Due to outstanding properties and capabilities of BTO recently there have been many attempts to prepare various shapes and products of BTO$^{[5-8]}$. In optics, To meet the miniaturization, high transmittance nanothin films are required. In the literature, different approaches including electrodeposition$^{[9]}$, sputtering$^{[10]}$, plasma-enhanced PVD$^{[11]}$, hydro and solvothermal$^{[12,13]}$ and sol-gel processing methods$^{[14-19]}$ were utilized to obtain BTO coatings. Dip-coating approach and sol-gel processing method are desirable options for obtaining BTO thin uniform coating$^{[20-22]}$.

High transparency quality is one of the most importance requirements in many optical applications. In this way, preparing high transmittance films can lead to improvement in the optical devices based on BTO. In this research, BTO thin coatings are applied on the soda-lime glass substrate using dip-coating approach. Optical responses of the BTO thin coating and effect of preparing parameters on BTO thin coating transparency are characterized. Results indicate the outstanding transparency as a key property of prepared BTO thin coatings.

2. Materials and Methods

The precursors used in this research for obtaining the BTO...
colloidal sol are mentioned elsewhere\textsuperscript{7}. The BTO colloidal sol was prepared using acetic acid, barium acetate, TTIP, 2-propanol and deionized water with 6:1:1:1:150 molar ratios (Figure 1). BTO thin coatings were obtained by dipping the glass substrate in the BTO colloidal sol. The coated glass were then dried at 100 °C and afterward were calcined at 500 °C. The prepared BTO thin coating are characterized by optical spectroscopy, fourier transform infrared (FT-IR) spectroscopy. The structural characterizations were carried out by TGA, XRD, DEK-TAK, SEM, TEM and AFM.

Figure 1. Sol preparation method and coating stages

3. Results and Discussion

In this research, BTO thin coatings were synthesized at low temperature in a relatively short period of time through a newly developed sol-gel processing method. For this purpose, the hydrolysis conditions were modified according to the procedure that is shown in Figure 1. In contrast to many previous researches\textsuperscript{1,20,23-26}, we used a two-step, hydrolysis at low temperature, least possible amounts of acetic acid and 2-propanol. In these conditions, much deionized water was added to the precursor mixture. Unlike other reports, acetyl acetone was not used as the modifier in the precursors\textsuperscript{20,26}. These conditions have great effects on lowering the synthesis temperature and time. On the other hand, the cost of preparation is significantly reduced in contrast to the literature\textsuperscript{1,27}. Meanwhile the sol is prepared quickly in 90 minutes. Other researchers spent very long time on sol preparation (e.g. more than 8 h)\textsuperscript{1,23}. Hence, the process developed here is cost-effective and therefore can be serving, as is a good candidate for mass production. The prepared sol has enough stability and is stable for at least three months. Figure 2 shows the sol appearance with the time of the as-prepared colloidal sol during its lifetime and clearly shows sol to gel transformation.

Figure 2. The change in the sol appearance with time

FT-IR spectrum of the sol is presented in Figure 3. The peak at 3467 cm\textsuperscript{-1} is attributed water in the sol. Reflection at 3176 cm\textsuperscript{-1} is assigned to C-H functional group. The reflection at wavenumber of 1640 cm\textsuperscript{-1} is related to BTO\textsuperscript{28}. The doublet bands at 1560 cm\textsuperscript{-1} and 1410 cm\textsuperscript{-1} are assigned to carboxylate functional groups induced by acetic acid\textsuperscript{20}. The reflection at 1040 cm\textsuperscript{-1} is attributed to alcoholic C-O functional groups, and the reflections at 950, 840, 770, 670, 550 and 480 cm\textsuperscript{-1} are due to M-O bonds\textsuperscript{20,29}. The broadening of the FT-IR reflection at wavenumber range of 770-840 cm\textsuperscript{-1} is assigned to complexes of Ba and Ti. The functional groups at 550 and 670 cm\textsuperscript{-1} are attributed to Ti-O band. The peak at 480 cm\textsuperscript{-1} is assigned to Ti-O-Ti band\textsuperscript{30,31}.
Thermogravimetric (TGA) analysis of the colloidal sol after its drying is presented in Figure 4. This figure indicates that the dried gel experiences 40% weight loss totally. The successive steps of weight loss include a weight loss step at temperature range of 50-240 °C mainly attributed to evaporation of volatile materials, a weight loss at the temperature range of 240-570 °C is due to the pyrolysis of the Ba-Ti complexes and the final weight loss step at the temperature range of 570-770 °C is mainly due to BTO formation from the reaction of barium carbonate and TiO$_2$. X-ray diffractometry results of the BTO coating after 1 hour firing at 500 °C is presented in Figure 5 indicating the amorphous nature of obtained BTO thin coating.

The optical properties of the uncoated substrate and the coated one are shown in Figure 6 indicating the better optical response of the obtained thin BTO coating in contrast to the literature$^{[4,19,32]}$. It is seen that the deposited BTO thin coating presents the high transmittance quality in the wavelengths of 400 to 1200 nm. With a mean transmission of 86.5% in the mentioned range which is much more than the similar works$^{[4,19,32]}$ with a mean transmittance of 70-75%. As shown in Figure 7a the incident light to the BTO coating is divided to three portions including absorption, reflection and transmittance$^{[33,34]}$. This figure clearly shows the high transparency of the deposited coating. Following the method published in the literature$^{[4,19,32]}$ and optical response of the film the bandgap of the film was calculated to be 3.9 eV (see Figure 7b).
Figure 7b. The variation of \((ahv)^2\) versus photon energy \(hv\) for BaTiO\(_3\) nanothin film

Figure 8a presents atomic force microscopy micrograph of the thin BTO coating. It is seen from this micrograph that the surface of the coating has a dense amorphous texture without presenting the crack and voids. On the other hand, RMS roughness of the thin BTO coating is about 0.743 nm which approves the smoothness of the coating. The smoothness of the thin BTO coating can result in a decrease in the optical losses and thus high transparency quality in the BTO thin coatings in contrast to the crystalline and thick films\(^{[4,19,32]}\). Figure 8b shows SEM micrograph of a coated sample. It is seen that no grain has been formed on the surface of the film indicating the amorphous nature of the BTO film.

Figure 8b. SEM micrograph of BaTiO\(_3\) nanothin film

In the dip-coating technique the thin films are formed after dipping and withdrawal the substrate in sol and after drying and firing the thin films is prepared. In Figure 11 and Figure 12, effect of withdrawal rate on transmission spectrum and film thickness has been evaluated. Results show that thin film thickness increases and the transparency decreases with increment of withdrawal rate. At lower withdrawal rate, draining of the sol, leads to a decrease
in the film thickness. This fact leads to an increase in thin film transparency as well.

![Figure 11. Effect of withdrawal rate on thin film transparency](image1.png)

**Figure 11.** Effect of withdrawal rate on thin film transparency

![Figure 12. Effect of withdrawal rate on thin film thickness](image2.png)

**Figure 12.** Effect of withdrawal rate on thin film thickness

### 4. Conclusion

This work reports a sol-gel routine to obtain high transmittance BTO thin coatings. The prepared BTO thin coating exhibits less optical losses in contrast to the polycrystalline BTO coating explored in the literature. AFM results indicate the nanoscale smoothness of the coating leading to high transparency quality of the deposited BTO thin coating. Results also indicate that increment of the calcination temperature and withdrawal rate reduces the thin films transparency. Finally, the results advocate the outstanding transparency as a key property of the prepared BTO thin coating.

### References


[34] XU, Zh., Optical properties of amorphous Ba0.7Sr0.3TiO3 thin films oBTO ained by metal organic decomposition technique, Thin Solid Films, 2006, nr. 515, page 2326.