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Dielectric Properties of Nanostructured $Bi_4Ti_3O_{12}$ and $Bi_{12}TiO_{20}$ Films Prepared by Sol-Gel Method

A. Sadeghzadeh-Attar[1]

1- Introduction

In recent years, ferroelectric materials due to their good dielectric properties have received considerable attention for many applications in nonvolatile electronic and electro-optical devices. Layered compounds were studied for the first time by Bengt Aurivillius, who discovered a new phase with layered structure in the Bi_2O_3-TiO_2 system. He described the structure as formed by bismuth oxide based layered interleaved with pseudo-perovskite type layers. In the general formula of the Aurivillius family, $(Bi_2O_2)^{2+}(A_{m-1}B)_mO_{3m+1})^{2-}$, A is a large 12 co-ordinate cation, B is a small 6 co-ordinate cation, and m is an integer named integration factor between 1 to 8. Several phases in the Bi-Ti-O system can be formed, such as $Bi_4Ti_3O_{12}$, $Bi_{12}TiO_{20}$, $Bi_2Ti_2O_7$, $Bi_2Ti_4O_{11}$, Bi_8TiO_{14}, $Bi_{20}TiO_{32}$, and so on. Among them, Bi_4TiO_{12} and $Bi_{12}TiO_{20}$ are the best known compounds, attracted great interest duo to their possible applications in optical devices and ferroelectric memories transducers, capacitors, and acoustic piezo-sensors. Many techniques have been employed for preparing a layered structure of bismuth titanate phases including chemical vapor deposition (CVD), pulse laser deposition, magnetron sputtering, atomic layer deposition, sol-gel synthesis, and others. Between them, sol-gel method gives the possibility for fabrication of complex and homogeneous compounds, easy control of the process, synthesis at low temperature, and low cost. The purpose of the present work is to synthesize and characterize nanostructured $Bi_4Ti_3O_{12}$ and $Bi_{12}TiO_{20}$ films by sol-gel method and to study their dielectric properties depending on annealing temperature and applied frequency.

2- Experimental

Bismuth titanate ($Bi_4Ti_3O_{12}$ and $Bi_{12}TiO_{20}$) films were prepared by sol-gel method using bismuth nitrate pentahydrate [$Bi(NO)_3.5H_2O$] and titanium isopropoxide [$Ti(OCH(CH_3)_2)_4$] as starting materials. Glacial acetic acid was used simultaneously as solvent and catalyst. Ethanol was used as solvent. In order to prepare stable mixtures, the Ti ions were connected in stable

complexes with acetylacetone [$C_5H_8O_2$] with a ratio of 1:3. The typical procedure was as follows: initially, a transparent solution was formed by dissolving bismuth nitrate in glacial acetic acid and deionized water according to the relevant stoichiometric ratio and stirring for several minutes at room temperature. Subsequently, the mixture of titanium isopropoxide, ethanol and acetylacetone was slowly added into the above solution under constant stirring. The obtained sols were dip coated onto the glass slide substrates by using a dip coater at the rate of 2 mm/s. After dip coating the substrates, the films were kept at 100 ºC for 2 h. Heat treatment of dried films was carried out in a furnace at the temperature range from 300-700 ºC for 1 h to promote the crystallization of the samples. The crystal structure of annealed films was examined by X-ray diffraction (XRD) using a Philips X'Pert X-ray diffractometer. FT-IR spectra for samples with different annealing temperatures were carried out using a FTIR spectrometer (model; Bruker TENSOR 27). Field emission scanning electron microscope (Hitachi S4160) equipped with energy-dispersive X-ray spectroscopy (EDS) was used to study the surface morphology and chemical composition of the films. Dielectric constant and loss of samples were measured using a LCR meter (model INSTEK LCR-821). Prior to studying the dielectric properties, a thin layer of silver was deposited by direct current sputtering on top and bottom of the glass slide as electrode. The dielectric constant ε for the investigated samples was measured at ambient temperature in the 1, 10, 100, and 1000 KHz frequency.

3- Results and Discussion

Fig. 1 shows IR spectra of the as-prepared and annealed $Bi_4Ti_3O_{12}$ and $Bi_{12}TiO_{20}$ samples, respectively. The broad band around 3000-3500 cm^{-1} was due to O-H stretching vibrations of the hydroxyls. This bond decreased in intensity with increasing heating and disappeared after calcination at 400°C. The bands in the region of 1500-1600 cm^{-1} were attributed to the formation of acetylacetanate ligands. It can be observed that the absorption bands in the range of below 900 cm^{-1} can be attributed to the Bi-O and Ti-O vibrations.

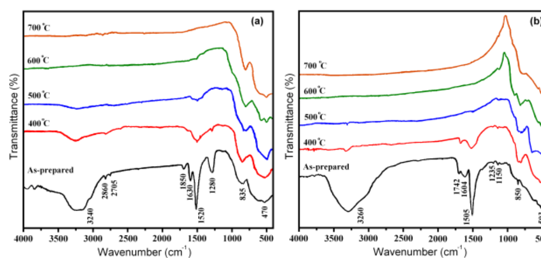

Fig. . IR spectra of the as-prepared and annealed samples; a) $Bi_4Ti_3O_{12}$ and b) $Bi_{12}TiO_{20}$

Fig. 2 illustrates XRD patterns of $Bi_4Ti_3O_{12}$ and $Bi_{12}TiO_{20}$ samples annealed at various temperatures for 1 h. The XRD pattern in Fig. 2a shows that the peaks of TiO_2 and Bi_2O_3 completely disappeared at 600 ºC. The intensity and position of peaks corresponding to $Bi_4Ti_3O_{12}$ single phase with orthorhombic crystal structure without second phase corresponding to JCPDS card number: 0213-12. The XRD pattern shown in Fig. 2b confirms the formation of $Bi_{12}TiO_{20}$ with the cubic crystalline phase at 600 °C in accordance with standard card JCPDS: 0097-34. The intensity of peaks decreased with increasing annealing

[1] Assistant Professor, Department of Metallurgy and Materials Engineering, University of Kashan, P.O. Box. 87317-53153, Ghotb Ravandi Blvd., Kashan, Iran.

temperature, which is an indicative of higher crystallinity and larger particle size.

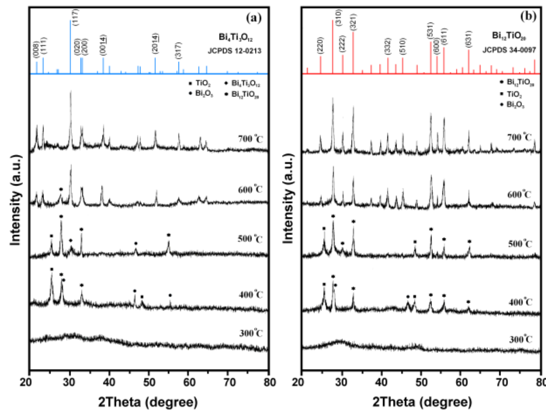

Fig. 2 The XRD patterns of a) $Bi_4Ti_3O_{12}$, b) $Bi_{12}TiO_{20}$ samples annealed at various temperatures for 1 h

Fig. 3 indicates FESEM images of nanostructured $Bi_4Ti_3O_{12}$ and $Bi_{12}TiO_{20}$ films annealed at 600 °C for 1 h. It can be found that the surface of films is uniform and smooth without any crack. Bi, Ti, and O elements were detected in both samples correlated to the formation of stoichiometric $Bi_4Ti_3O_{12}$ and $Bi_{12}TiO_{20}$ compositions.

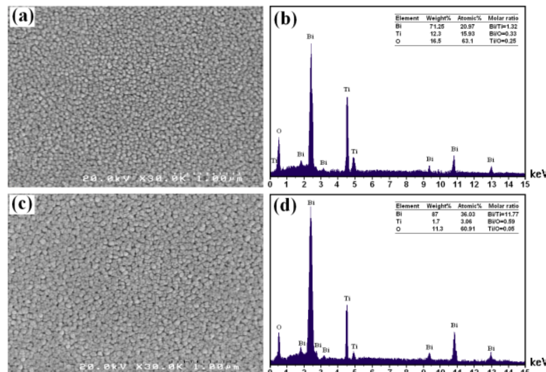

Fig. 3 FESEM images of the a) $Bi_4Ti_3O_{12}$, and c) $Bi_{12}TiO_{20}$ samples annealed at 600 °C for 1 h. EDS analysis of the b) $Bi_4Ti_3O_{12}$, and d) $Bi_{12}TiO_{20}$ samples

Fig. 4 and Fig. 5 show the temperature dependence of dielectric properties for $Bi_4Ti_3O_{12}$ and $Bi_{12}TiO_{20}$ films measured at various frequencies. It is found that with increasing annealing temperature, dielectric constant and dielectric loss increases in both samples. Also, with increasing frequency, dielectric constant reduces and dielectric loss of the samples increases due to molecular polarization. As can be seen in these curves, frequency and annealing temperature have different effects on the dielectric properties. Therefore, these parameters should be considered prior to selecting the effective piezoelectric material.

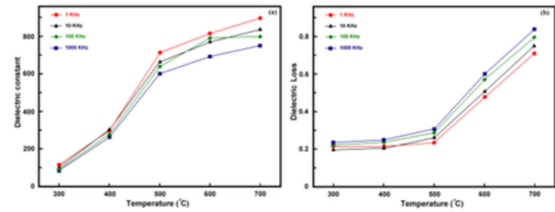

Fig. 4 Values of dielectric constant and dielectric loss at various frequencies plotted as a function of annealing temperature for $Bi_4Ti_3O_{12}$ sample

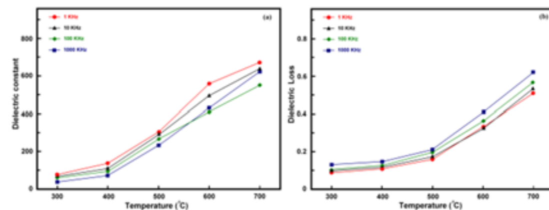

Fig. 5 Values of dielectric constant and dielectric loss at various frequencies plotted as a function of annealing temperature for $Bi_{12}TiO_{20}$ sample

4- Conclusions

Nanostructured bismuth titanate ($Bi_4Ti_3O_{12}$, $Bi_{12}TiO_{20}$) films were successfully fabricated via sol-gel method on the glass substrate. The structure and dielectric properties of the prepared thin films as a function of annealing temperature and applied frequency were also investigated. It was found from XRD patterns that the single phase were formed when $Bi_4Ti_3O_{12}$ and $Bi_{12}TiO_{20}$ samples was annealed at 600 ºC for 1 h. Therefore, optimal condition could be suggested at this temperature. FESEM images demonstrated that the surface of the films has a smooth and dense morphology. Dielectric studies show that the dielectric constant and loss factor increased with increased annealing temperature. Also, the values of dielectric constant of samples decreased and dielectric loss increased with increasing frequency.