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Effect of the excess of bismuth on the morphology and properties of the $BaBi_2Nb_2O_9$ thin films

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Abstract

In this study, the effect of bismuth content on the crystal structure, morphology and electric properties of barium bismuth niobate ($BaBi_2Nb_2O_9$) thin films was explored with the aid of X-ray diffraction (XRD), scanning electron microcopy (SEM), atomic force microscopy (AFM) and dielectric properties. $BaBi_2Nb_2O_9$ (BBN) thin films have been successfully prepared by the polymeric precursor methods and deposited by spin coating on Pt/Ti/SiO_2/Si (1 0 0) substrates. The phase formation, the grain size and morphology of the thin films were influenced by the addition of bismuth in excess. It was observed that the formation of single phase BBN for films was prepared with excess of bismuth up to 2 wt%. The films prepared with excess of the bismuth showed higher grain size and better dielectric properties. The 2 wt% bismuth excess BBN thin film exhibited dielectric constant of about 335 with a loss of 0.049 at a frequency of 100 kHz at room temperature.

Keywords: A. Films; B. Grain size; C. Dielectric properties; D. Niobates

1. Introduction

The bismuth layered structure perovskites have attained considerable importance owing to their potential ferroelectric non-volatile random access memories (NvRAM) applications apart from piezo- and pyro-electric-based sensor applications. The most interesting aspect of these materials has been their fatigue resistance against polarization switching, unlike the commercially popular ferroelectrics such as lead zirconate titanate (PZT) which loses its initial polarization after 10^6–10^8 switching cycles [1]. Although, significant amount of work has been devoted to the studies on Sr-based $n = 2$ members of the Aurivillius family of oxides such as $SrBi_2Ta_2O_9$ (SBT) and $SrBi_2Nb_2O_9$ (SBN) [2–5], their Ba counterparts, such as $BaBi_2Ta_2O_9$ (BBT) and $BaBi_2Nb_2O_9$ (BBN), have received much less attention perhaps owing to the difficulties in obtaining exact stoichiometric compositions as well as their decomposition nature at higher temperatures. Recent studies on BBT thin films demonstrate their excellent fatigue endurance with no polarization fatigue up to 10^{12} cycles [3]. The ferroelectric studies pertaining to BBN ceramics demonstrate its relaxor nature [6,7].

Despite of Ba-based counterparts are of great interest; there is a few reports about the synthesis of the thin films. Regarding BBN, thin films have been obtained by pulsed-laser ablation [8], RF-magnetron sputtering [9] and metal-organic decomposition (MOD) process [10].

The phase formation temperature, chemical homogeneity phase purity and electrical properties of multi-component electroceramic materials like BBN are highly dependent on the cation homogeneity in the oxide precursor [11]. An excess amount of Bi in layered structure perovskites is known to affect the ferroelectric properties, as well as the crystallographic structure [12,13]. Lua and Wen [14] observed that an excess amount of bismuth contents (10 mol%) in BBT thin films substantially further improves their ferroelectric properties and to prevent the evaporation of Bi from bulk surface [15,16]. However, it has been verified that too much Bi excess degrades the properties of the film as a consequence of Bi_2O_3 segregation from the matrix. For this, to control of Bi composition during

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the crystallization process is found to be important in obtaining better electrical properties [14].

In the present work, we report the role of Bi ions on the structural, morphological and electrical properties of $BaBi_2Nb_2O_9$ thin films obtained by polymeric precursor method.

2. Experimental procedure

BBN thin films were prepared by precursors polymeric decomposition process [17]. Barium acetate ($Ba(OOCCH_3)_2$, Merck), bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$, Mallinckrodt), niobium ethoxide ($Nb(OC_2H_5)_5$, AlfaAesar) were used as starting reagents. Barium acetate and bismuth nitrate pentahydrate were dissolved in an aqueous solution with citrate acid and the pH of the solution was adjusted between 7 and 8 with addition of NH_4OH. Then, 2-ethanediol was added to the solutions aiming to obtain the citrate solutions. In case of the niobium citrate, the niobium ethoxide was added to a solution of 1.2-ethanediol under heating and stirring. After this, citric acid was added to solution aiming to obtain the citrate solution. The solutions obtained were characterized by gravimetric analyses. The BBN solutions were prepared by mixing appropriated quantities of barium, bismuth and niobium citrates under stirring at 90 °C. After mixing, the BBN solution viscosity was adjusted at 20 cP by addition of water and by measuring using a Brookfield viscosimeter.

The thin films were deposited by a spin coating process on the platinum coated silicon substrates ($Pt/Ti/SiO_2/Si$). It was deposited a BBN layer with the spin coating operating at 3000 rpm for 30 s. After spin coating, the films were kept on a hot plate at 90 °C in air again, for the elimination of water and the excess of 1.2-ethanediol. The above steps were repeated until a 300 nm thickness thin film was obtained. Then, the films were annealed in flowing oxygen in two steps, first the heating rate was 2 °C/min up to 300 °C to remove organic material and second the heating rate was increased to 5 °C/min up to 700 or 800 °C to promote phase crystallization. These conditions were used to obtain crack-free films.

Phase formation was performed at room temperature by X-ray diffraction using a BraggBretano diffratometer (Siemens D-5000) and Cu K_α radiation. The surface morphology and roughness were measured by atomic force microscopy (Digital, NanoScope 3A) using tapping mode with amplitude modulation. It was utilized a Silicon Nitride triangular shaped (Digital Instruments) as a tip. The images were obtained in a 1 μm^2 area, 512 pixel por line and 1 Hz. The grain size was obtained by the interceptors' method [17] in 2D views of the AFM images. The results obtained represent an average value of six measurements. The relative dielectric constant (ε) and dissipation factor ($\tan\delta$) were measured versus frequency using an impedance analyzer (Model 4194A, Hewlett Packard).

3. Results and discussion

The XRD data obtained for pure BBN thin films heat treatment at 700 °C for 1 h and with different excess of bismuth are shown are shown in Fig. 1. It can be observed that the addition of 5 mol% bismuth excess leads to the formation of secondary phases, $Bi_2Nb_{10}O_{28}$ and $BiNbO_4$, in the thin films that can degraded the electrical properties.

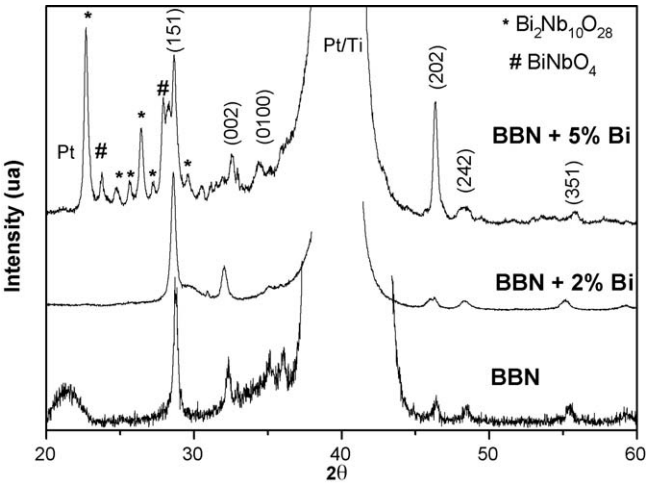


Fig. 1. XRD obtained for stoichiometric, 2 and 5 mol% Bi excess BBN thin films annealed in oxygen flow at 700 °C for 1 h.

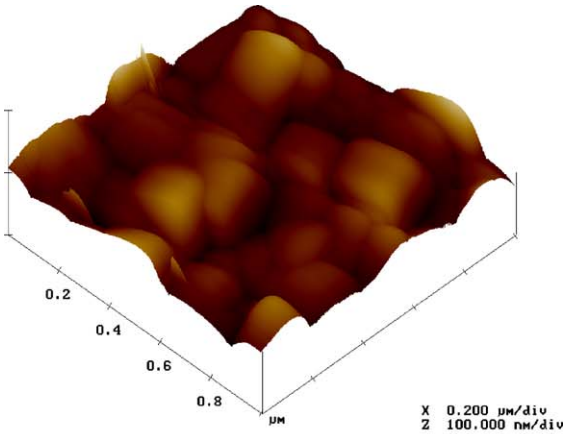
Table 1
RMS and grain size values obtained for stoichiometric and 2 and 5 mol% Bi excess BBN thin films annealed in oxygen flow at 700 °C for 1 h.

Samples	RMS (nm)	Grain size (nm)
BBN	11.2	240–270
BBN + 2% Bi	8.7	250–280
BBN + 5% Bi	6.7	400–500

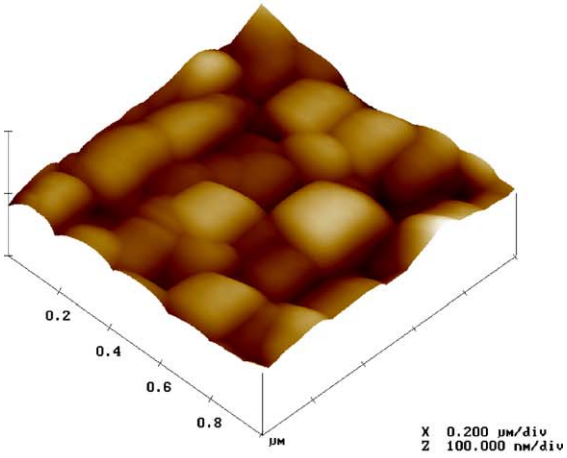
The influence of the use of bismuth excess on microstructure was verified by results of AFM (Fig. 2), grain size and RMS surface roughness values (Table 1) obtained for the thin films without and with Bi excess. Comparing the micrographs obtained by AFM for pure and 2 or 5 mol% Bi excess BBN thin films, it can be noticed (Fig. 2) that the use of Bi excess influenced on the microstructure of the films. The grain size is bigger and the roughness is lower compared to those of the BBN films prepared with Bi excess (Table 1).

BBN thin films prepared with Bi excess showed rather dense, smooth and with a microstructure homogeneous (Fig. 2). Although, the BBN thin films prepared with addition of 5 mol% Bi excess showed an homogeneous microstructure, the results obtained by XRD (Fig. 1) show the formation of secondary phases. These suggest that the best concentration of Bi excess is 2 mol%.

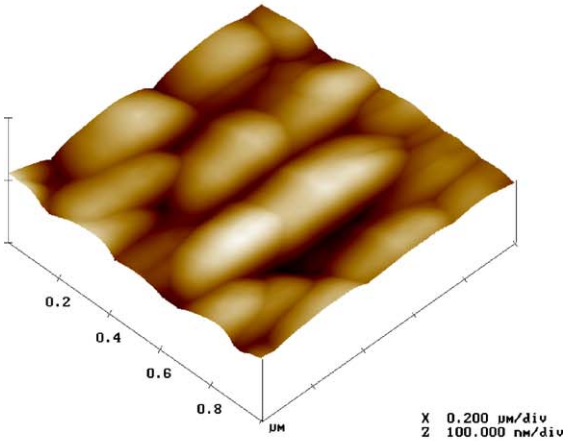
The dielectric constant versus frequency and dissipation factor versus frequency plots obtained for pure, 2 and 5 mol% of BBN thin films are showed in Figs. 3 and 4. The dielectric constant and dissipation factor obtained at 100 kHz at room temperature for different BBN films are showed in Table 2. It can be verified that the addition of Bi excess aided to obtain BBN thin films with better dielectric properties. This result can be explained because the films prepared in this way present a more homogeneous microstructure and higher densities. The



(a) BBN p



(b) 2 mol% Bi excess



(c) 5 mol% Bi excess

Fig. 2. 3D views AFM images obtained for stoichiometric, 2 and 5 mol% Bi excess BBN thin films annealed in oxygen flow at 700 °C for 1 h.

thin films prepared with 5 mol% Bi excess, which had crystallized secondary phases, presented lower values for dielectric properties than the films prepared with 2 mol% Bi excess, indicating that these phases degrades the dielectric

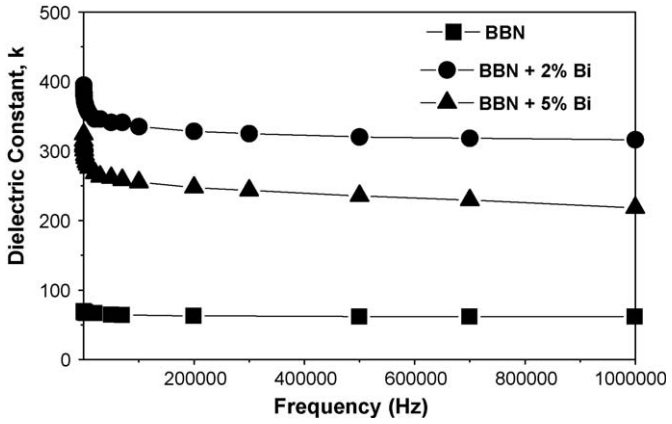


Fig. 3. Dielectric constant versus frequency for stoichiometric, 2 and 5 mol% Bi excess BBN thin films annealed in oxygen flow at 700 °C for 1 h.

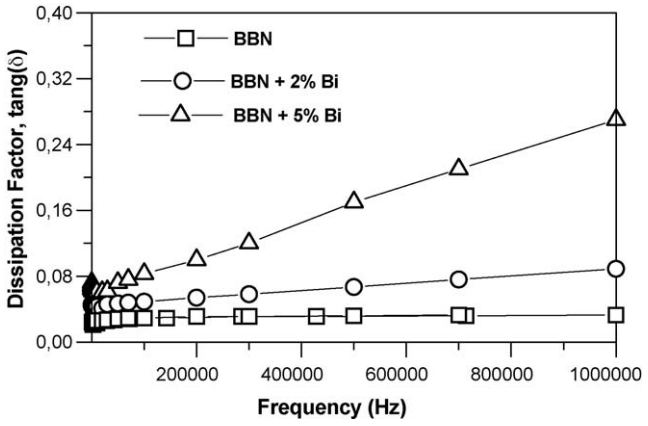


Fig. 4. Dissipation factor versus frequency for stoichiometric, 2 and 5 mol% Bi excess BBN thin films annealed in oxygen flow at 700 °C for 1 h.

Table 2
Dielectric constant and dissipation factor obtained at room temperature at 100 kHz, for stoichiometric and 2 and 5 mol% Bi excess BBN thin films prepared in different conditions.

Sample	Temperature	Dielectric constant (ε)	Dissipation factor (tan(δ))	ε and tan(δ) according to literature
BBN	700 °C/1 h	63	0.031	No found
BBN + 2% Bi	700 °C/1 h	335	0.049	214 e 0.04[8]
BBN + 5% Bi	700 °C/1 h	255	0.083	No found

properties of the BBN. This demonstrates that there is an optimum concentration of bismuth to obtain thin films with homogeneous microstructure, without secondary phases and better electrical properties.

In Fig. 4, it is possible to observe a slight increase in the dissipation factor at high frequencies. Probably, this behavior results from the interaction between the Pt/BBN interfaces.

The better dielectric constant value obtained in this work was 335 with dissipation factor around 0.04. These values were better than the values reported until now [8–10]. This confirms the efficiency of addition of Bi in excess to control the

microstructure and to improve the dielectric properties of BBN thin films.

4. Conclusions

BBN thin films were successfully prepared on Pt/Ti/SiO_2/Si substrates by polymeric precursor method. The BBN phase was obtained by annealing at 700 °C. The addition of excess Bi influenced the microstructure and dielectric properties of the films. The surface of the prepared films with addition of Bi excess was rather dense and smooth with no cracks. The film prepared with 2 mol% Bi excess annealed at 700 °C for 1 h exhibited a room temperature dielectric constant of about 335 with a dissipation factor of 0.049 at a frequency of 100 kHz.

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References

[1] C.A.P. de Araujo, J.D. Cuchiaro, I.D. McMillan, M.C. Scott, J.F. Scott, Fatigue-free ferroelectric capacitors with platinum-electrodes, Nature 374 (1995) 627.
[2] P. Tejedor, C. Ocal, E. Barrena, R. Jiménez, C. Alemany, J. Mendiola, Composition-related effects of microstructure on the ferroelectric behavior of SBT thin films, Appl. Surf. Sci. 175 (2001) 759.
[3] A.Z. Simões, G.C.C. da Costa, M.A. Ramírez, J.A. Varela, E. Longo, Effect of the excess of bismuth on the morphology and properties of the $BaBi_2Ta_2O_9$ ceramics, Mater. Lett. 59 (2005) 656.
[4] D. Debasis, G.K. Tanmay, P. Panchanan, Studies of dielectric characteristics of $BaBi_2M_2O_9$ ferroelectrics prepared by chemical precursor decomposition method, Solid State Sci. 9 (2007) 57.
[5] C.H. Lu, C.Y. Wen, New non-fatigue ferroelectric thin films of barium bismuth tantalate, Mater. Lett. 38 (1999) 278.
[6] C. Miranda, M.E.V. Costa, M. Avdeeev, A.L. Kholkin, J.L. Bapista, Relaxor properties of Ba-based layered perovskites, J. Eur. Ceram. Soc. 21 (2001) 1303.
[7] C. Karthik, K.B.R. Varma, Dielectric and pyroelectric anisotropy in melt-quenched $BaBi_2(Nb_{1-x}V_x)_2O_9$ ceramics, Mater. Res. Bull. 43 (2008) 3026.
[8] T. Mazon, E. Joanni, J.R.A. Fernandes, Growth and characterization of $BaBi_2Nb_2O_9$ thin films made by RF-magnetron sputtering, Ferroelectrics 293 (2003) 201.
[9] A. Laha, S.B. Krupanidhi, Growth and characterization of excimer laser-ablated $BaBi_2Nb_2O_9$ thin films, Appl. Phys. Lett. 77 (2000) 3818.
[10] A. Benan, P. Boullay, J.P. Mercurio, Characterization of $BaBi_2Nb_2O_9$ powders and thin films prepared by a solution synthesis technique, Solid State Sci. 6 (2004) 547.
[11] M. Kakihana, "Sol-gel" preparation of high temperature superconducting oxides, J. Sol-Gel Sci. Technol. 6 (1996) 7.
[12] T.C. Chen, T. Li, X. Zangh, S.B. Desu, Impedance spectroscopy of $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ ceramics correlation with fatigue behavior, J. Mater. Res. 12 (1997) 1569.
[13] J.K. Lee, S.J. Kim, K.S. Hong, Evolution of electrical properties for excess Bi_2O_3 content in $SrBi_2Ta_2O_9$ ceramics, J. Korean Phys. Soc. 35 (1999) 526.
[14] C.H. Lua, C.Y. Wen, Phase formation and ferroelectric characteristics of nonfatigue barium bismuth tantalate thin films, J. Appl. Phys. 86 (1999) 6335.
[15] C. Karthik, K.B.R. Varma, Influence of vanadium doping on the processing temperature and dielectric properties of barium bismuth niobate ceramics, Mater. Sci. Eng. B 129 (2006) 245.
[16] H.N. Lee, D. Hesse, N. Zakharov, U. Gosele, Ferroelectric Bi3.25La0.75-Ti3O12 films of uniform a-axis orientation on silicon substrates, Science 296 (2002) 2002.
[17] M.P. Pehini, U.S. Patent No. 3,330,697 (1967).