Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Compensation for volatile elements to modify the microstructure and energy storage performance of (W,Ni)-codoped $Na_{0.5}Bi_{0.5}TiO_3$ ceramic films

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ARTICLE INFO

Keywords:
Ferroelectric
Film
Nonstoichiometry
Microstructure
Energy storage

ABSTRACT

This work reports the characteristics of nonstoichiometric $Na_{0.5+x}Bi_{0.5+y}Ti_{0.96}W_{0.01}Ni_{0.03}O_3$ (x = 0.0%, y = 1.0%; x = 0.5%, y = 2.0%; x = 1.0%, y = 4.0%) ceramic films derived from chemical solution deposition and the role played by excess Na/Bi in modifying microstructure and electrical properties. Single perovskite phase structure can be maintained in all compositions. Decreased grain size can be obtained with the increasing compensation for volatile Na/Bi elements. Particularly, extra amounts of 0.5 mol% Na and 2.0 mol% Bi leads to reduced leakage and enhanced ferroelectric polarization. Meanwhile, due to the high breakdown electrical field strength and large difference between maximum and remanent polarization, an excellent energy storage performance can be achieved in $Na_{0.505}Bi_{0.52}Ti_{0.96}W_{0.01}Ni_{0.03}O_3$ sample, which is distinguished by a recoverable energy storage density of 40.5 J/cm^3 and an energy storage efficiency of 43.6% at 2515 kV/cm as well as a good frequency stability. Hence, the regulation for the content of volatile elements is effective to modify the electrical response of $Na_{0.5}Bi_{0.5}TiO_3$-based materials.

1. Introduction

As the global energy issues are pushed into the spotlight, the demand of high-performance energy storage materials is increasingly urgent. It is classically accepted that the recoverable energy storage density (W) of dielectrics can be calculated through the integration of polarization-electric field (P-E) data using a mathematical method [1]:

$$W = \int_{P_r}^{P_{max}} EdP \quad (1)$$

where E is applied electric field, P is polarization, P_{max} and P_r are the maximum and remanent polarization. With a view to the formula above, a high W is not only related to a high breakdown electrical field strength (BDS) but also dependent on a large difference between P_{max} and P_r (P_{max}-P_r), which provides a train of thought for designing dielectric materials with high energy storage property [2,3].

At present, the lead-free dielectric materials, represented by $BaTiO_3$ (BT), $(Ba,Ca)(Zr,Ti)O_3$, $Ba_{0.4}Sr_{0.6}TiO_3$ and $Na_{0.5}Bi_{0.5}TiO_3$ (NBT)-based ceramics etc., are being extensively investigated due to the advantage of high energy storage efficiency (η) combined with environmental friendliness [4–7]. Among these promising lead-free energy storage material systems, NBT is a typical perovskite-type ferroelectric with A-site being equally occupied by Na^+ and Bi^{3+}, researches about which have been conducted for application in energy storage devices [3,7,8]. Compared with bulk materials, films endow with lower size and higher BDS, which is no doubt conducive to the future development of microelectronic devices. In line with this, pure NBT film with good energy storage performance (W = 12.4 J/cm^3 and η = 43% at 1200 kV/cm) was successfully prepared by Zhao et al. [9]. Zhang et al. reported that high BDS and P_{max}-P_r values led to enhancement in energy storage property (W = 2.3 J/cm^3 and η = 45% at 550 kV/cm) by moderate BT addition in NBT film [10]. Our previous work also probed into a feasibility of energy storage application for NBT-based film through modification with 1 mol% W^{6+} and 3 mol% Ni^{2+} (W = 15.1 J/cm^3 and η = 34.9% at 1753 kV/cm) [11]. Thus, there is some reason to believe that the energy storage performance is susceptible to compositional variations in NBT-based material systems.

However, it must be kept in mind that the volatilization of A-site elements (Na & Bi) during the high-temperature crystallization process brings about the compositional variation, i.e. forming sodium vacancies (V'_{Na}) and bismuth vacancies (V''_{Bi}) and accordingly generating oxygen vacancies ($V_O^{\bullet\bullet}$). Reactions proceed by:

$$2Na_{Na}^{\times} + O_O^{\times} \rightarrow 2V'_{Na} + V_O^{\bullet\bullet} + Na_2O \quad (2)$$

$$2Bi_{Bi}^{\times} + 3O_O^{\times} \rightarrow 2V''_{Bi} + 3V_O^{\bullet\bullet} + Bi_2O_3 \quad (3)$$

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https://doi.org/10.1016/j.ceramint.2018.05.153
Received 24 March 2018; Received in revised form 12 May 2018; Accepted 17 May 2018

Unfortunately, the generated free $V_O^{\cdot\cdot}$ in ferroelectric film is detrimental to film resistivity, which will cause reduction in BDS and polarization, limiting the development in practical application [12,13]. In this regard, an usual routine is adding excess Na/Bi-containing starting materials to compensate for the potential loss, elevating electrical properties in NBT-based materials. For example, the 0.97NBT-0.03$BiAlO_3$ film processed with 10 mol% excess sodium acetate and 2 mol% excess bismuth nitrate pentahydrate exhibited reduced leakage current density ($\sim 10^{-6}$ A/cm^2 at 200 kV/cm) and enhanced ferroelectricity ($P_r \sim 16.5$ μC/cm^2) [14]. Besides, high saturation polarization ($P_s \sim 23$ μC/cm^2) and remanent polarization ($P_r \sim 12$ μC/cm^2) values were achieved in NBT-BT film prepared by the solution containing 10 mol% excess sodium acetate trihydrate and 10 mol% excess bismuth acetate [15]. It was also reported that good energy storage performance ($W = 2.7$ J/cm^3 and $\eta = 45\%$ at 600 kV/cm) was obtained in 0.7NBT-0.3$SrTiO_3$ film with extra amounts of 2 mol% Na and 5 mol% Bi added in the form of sodium carbonate and bismuth oxide [16]. Therefore, it is crucial to systematically explore the impacts of excess Na/Bi addition on the electrical properties of NBT-based materials.

Here, we present our studies of (W,Ni)-codoped NBT (NBTWN) ceramic films from the standpoint of A-site nonstoichiometry, emphasising the effects of Na/Bi excess on their microstructure and energy storage performance. Results show a well maintained polycrystalline perovskite structure in each sample and an optimized energy storage performance with large W of 40.5 J/cm^3 and high η of 43.6% in the film modified by extra 0.5 mol% Na and 2.0 mol% Bi.

2. Experiment

$Na_{0.5+x}Bi_{0.5+y}Ti_{0.96}W_{0.01}Ni_{0.03}O_3$ (abbreviated as $Na_{0.5+x}Bi_{0.5+y}$TWN; x = 0.0%, y = 1.0%; x = 0.5%, y = 2.0%; x = 1.0%, y = 4.0%) ceramic films were grown on indium tin oxide (ITO)/glass substrates by chemical solution deposition. The analytical reagents, including sodium acetate, bismuth nitrate pentahydrate, titanate isopropoxide, tungstenic acid and nickel acetate tetrahydrate, serve as source materials. First, to ensure the stability of Ti, titanate isopropoxide was reacted with acetylacetone in a molar ratio of 1:2. Then, the Na, Bi, W and Ni-containing raw materials were dissolved in the mixed solvents of ethylene glycol and acetic acid. Subsequently, the obtained complex system was carefully introduced into the stabilized Ti solution, following which 30% by weight of polyethylene glycol was added to form the final precursor solution with 0.3 M. Here, certain amounts of excess sodium acetate and bismuth nitrate pentahydrate were weighed and dissolved together with original amount according to the compositional requirement of $Na_{0.5+x}Bi_{0.5+y}$TWN (x = 0.0%, y = 1.0%; x = 0.5%, y = 2.0%; x = 1.0%, y = 4.0%). Each film was obtained by spin-coating on ITO/glass substrate, followed by drying at 300 °C for 5 min on a hot plate and annealing at 520 °C for 10 min in the rapid thermal processor. This processing was repeated several times to achieve the expected thickness.

The phase structures and morphologies of $Na_{0.5+x}Bi_{0.5+y}$TWN films were analyzed by X-ray diffractometer (XRD, Bruker D8) and scanning electron microscope (FeSEM, Hitachi S-4200). Top electrodes of Au were sputtered onto films surfaces for measuring electrical properties. The Keithley 4200 semiconductor characterization system was adopted to evaluate the insulating properties. And a standard ferroelectric tester (Precision Pro. Radiant Technologies) was utilized to test the ferroelectricity.

3. Results and discussion

The XRD patterns for Na/Bi nonstoichiometric NBTWN ceramic thin films deposited on ITO substrates are shown in Fig. 1. Subtracting the typical diffraction peaks of ITO, the single NBTWN phase can be identified, which belongs to the ABO_3 perovskite structure with the space group $R3c$. Moreover, there is no clear indication of secondary phase within the detection precision and resolution of the currently used XRD technique. Combined with the stoichiometric NBTWN in our previous work [11,17], the XRD analyses reveal a component flexibility of Na and Bi nonstoichiometry for the (W,Ni)-codoped NBT.

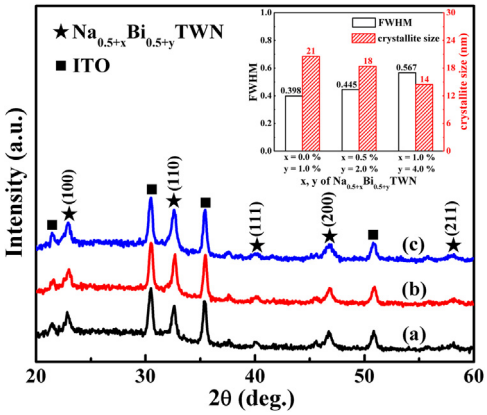

Fig. 1. XRD patterns of $Na_{0.5+x}Bi_{0.5+y}$TWN films: (a) x = 0.0%, y = 1.0%; (b) x = 0.5%, y = 2.0% and (c) x = 1.0%, y = 4.0%. The inset shows the FWHM and calculated crystallite size for the samples.

Based on the full width at half maximum (FWHM) of diffraction peak in XRD data, the average crystallite size can be evaluated by Scherrer formula [18]. The inset of Fig. 1 presents the values of FWHM of (110) peaks and calculated crystallite sizes for all the samples. As Na and Bi contents increase, it can be found that the FWHM value increases from 0.398 to 0.567. Accordingly, the calculated average crystallite size decreases from 21 to 14 nm. This can be regarded as a response to the suppressed concentration of $V_O^{\cdot\cdot}$, which is important for the transfer of mass and energy [19,20].

Fig. 2 displays the FeSEM images and statistical grain size analysis for NBTWN ceramic thin films with various Na and Bi contents. From the morphologies shown in Fig. 2(a)–(c), all the film samples exhibit relatively dense surfaces, with no large cracks coming into our sight. However, some tiny voids, inevitably generated during the process of pyrolysis and crystallization, are found to be scattered on the surfaces. Moreover, the grain tends to be smaller in size as Na/Bi contents increase. Clear interface between NBTWN film and ITO substrate can be observed in each sample from the cross-sectional micrographs in Fig. 2(d)–(f). And the thickness for each film is approximately 400 nm.

To make clear of the grain size for each sample from a quantitative perspective, Fig. 2(g)–(i) exhibits the histograms of grain size distribution, which are analyzed by 100 grains randomly selected from the surface morphologies and fitted into Gaussian distributions as shown by the solid line. For clarity, Table 1 provides a summary of average particle grain size (D) and some other parameters in NBTWN films. In contrast with the stoichiometric NBTWN (D = 55 nm) [11,17], the average particle grain size for $Na_{0.5}Bi_{0.51}$TWN, $Na_{0.505}Bi_{0.52}$TWN and $Na_{0.51}Bi_{0.54}$TWN are 53, 42 and 29 nm, respectively. Note that the value of grain size obtained from the FeSEM images is not equal to that of the crystallite size calculated from the XRD data because the average particle grains can be considered as clusters of even smaller crystal grains [18]. Moreover, along with the increase in Na/Bi contents, a decreasing tendency of the average grain size can be found.

To intuitively understand the suppression effect of Na/Bi compensation on free $V_O^{\cdot\cdot}$, Fig. 3 shows the structure schematic diagrams of $Na_{0.5+x}Bi_{0.5+y}$TWN. With the increasing extra amounts of Na/Bi filled in the vacancies of V'_{Na} and V''_{Bi} produced by volatilization during high-temperature processing, the generated $V_O^{\cdot\cdot}$ can be reduced correspondingly [Eqs. (2) and (3)], having impact on electrical properties.

Fig. 4(a) shows the leakage current density-electric field (J-E) characteristics for the NBTWN ceramic thin films with Na and Bi nonstoichiometry. For each sample, the J exhibits an obvious growing tendency as E increases. Such phenomenon is partly related to the more