



Influence of excesses of volatile elements on structure and composition of solution derived lead-free $(\text{Bi}_{0.50}\text{Na}_{0.50})_{1-x}\text{Ba}_x\text{TiO}_3$ thin films



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ABSTRACT

The preparation of $(\text{Bi}_{0.50}\text{Na}_{0.50})_{1-x}\text{Ba}_x\text{TiO}_3$ films requires a compositional/structural control, as they determine the functionality of these materials. We report a systematic compositional and structural analysis on $(\text{Bi}_{0.50}\text{Na}_{0.50})_{1-x}\text{Ba}_x\text{TiO}_3$ films fabricated by chemical solution deposition. The effects of incorporating Na(I) and Bi(III) excesses are analyzed through the comparison of the compositional depth profiles of stoichiometric films (BNBT) and films containing excesses (BNBTxs). Heterogeneous compositional profiles with larger bismuth content close to the substrate and thicker film-substrate interfaces are observed in BNBTxs, unlike stoichiometric films, which show atomic concentrations that correspond to the nominal composition of the precursor solution. Excesses induce structural differences in depth, observing a shift of the region of coexistence of rhombohedral and tetragonal phases (morphotropic phase boundary) toward higher x values and the formation of thick film-substrate interfaces. In contrast, stoichiometric films have homogeneous compositional and structural profiles with the MPB placed close to that described for bulk ceramics.

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1. Introduction

High performance piezoelectric ceramics, which are widely used in micro- and nano-electromechanical systems (MEMS and NEMS), are mainly based on the lead zirconate titanate $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, (PZT) [1,2]. The main concern over the use of this material is its environmental impact, related to the pollutant lead content. Thus, the search of lead-free alternatives is attracting much attention [3–5].

Among the lead-free materials, $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT) [6] is an example of a distorted perovskite where the charge difference between sodium and bismuth cations is large enough to provide an energy ordering in the system. This results in a complex nano-domain structure, which confers it a particular electric response [7].

The main drawbacks of BNT, which limit its applications, are the high conductivity and coercive field. These make difficult the

poling process and thus, modified BNT compositions are being used [8]. Among them, $(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ (BNBT) is considered an attractive system to be studied as it presents a morphotropic phase boundary (MPB), similarly to PZT, where the electromechanical properties are maximized [9].

The MPB can be defined as the composition at which a phase transition occurs between two adjacent crystalline phases that have equal Gibbs free energy [10]. The optimization of the ferro-piezoelectric properties at the MPB of BNBT was originally explained by the coexistence of tetragonal and rhombohedral phases [11]. However, the phase transformation seems to be promoted not only by the composition but also by the temperature or even by an electric field; in this way the MPB in BNBT materials could be modified during the poling process [12,13]. It has been reported that the phase transition at the MPB occurs through intermediate phases of monoclinic symmetry [14,15]. Furthermore, recently the structures observed at long-range order have been found to be different from those detected at short-range order (nano-scale) in nanostructured BNBT ceramics [16], which shows

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the complexity of the crystallographic structure of these compositions.

Besides, it has been reported that for compositions with x between 0.055 and 0.12 the BNBT solid solution exhibits a variety of different crystalline structures. This has caused some controversy, that has not been settled fully yet. For compositions between $x \sim 0.06$ and $x \sim 0.10$, a cubic phase (Pm $\bar{3}$ m space group) is determined by X-ray diffraction for unpoled BNBT [17,18]. This cubic structure is described as a multiphase system, which at short-range order is constituted by tetragonal nano-regions (P4bm space group) with antiferroelectric or ferroelectric response, and ferroelectric rhombohedral regions (R3c space group). This structural model is in agreement with the relaxor-ferroelectric behavior reported in the literature for these materials [19]. However, according to Jo et al., a structural evolution from rhombohedral R3c/R3m to tetragonal P4mm occurs in the compositional range of $0.055 < x < 0.100$ [20]. Free energies of these crystalline structures are very similar; thus, in BNBT bulk materials with close nominal compositions, different crystalline structures can be found. If the determination of crystalline structures seems not to be clarified in bulk materials, it becomes a challenge in polycrystalline thin films.

The need to integrate this lead-free piezoelectric material in microelectronic devices makes the fabrication of thin films essential. The high compositional control required to obtain films with compositions close to the MPB in these complex oxides makes chemical solution deposition (CSD) one of the most appropriate techniques to fabricate BNBT thin films [21]. For the processing it must be taken into account that the BNBT solid solution contains two elements of high volatility, Na(I) and Bi(III). Their loss by volatilization during any of the thermal processes needed in CSD disrupts the compositional balance of the thin films. In principle, high volatilization rates are expected due to the high surface/volume ratio inherent in thin films. Traditionally excesses of these two volatile elements are incorporated in the precursor solutions to compensate the loss during the films annealing [22–25]. It has been reported that the use of these excesses produces displacements of the MPB position for thin films [25] but the associated compositional and structural changes that lead to this shift are poorly understood.

Here, we show our recent results in solution derived $(\text{Bi}_{0.50}\text{Na}_{0.50})_{1-x}\text{Ba}_x\text{TiO}_3$ thin films, concerning the effects on their composition and crystalline structure produced by the use of Na(I) and Bi(III) excesses in the precursor. At the same time, we explore in depth the diversity of crystalline phases present in these films with compositions around the MPB. The study is carried out by Rutherford Backscattering Spectroscopy and X-ray diffraction for a wide range of x values (with x from 0.035 to 0.150), including those reported as being in the MPB region for bulk ceramics. The structure of the $(\text{Bi}_{0.50}\text{Na}_{0.50})_{1-x}\text{Ba}_x\text{TiO}_3$ thin films is studied in comparison with their counterpart bulk ceramics prepared following an identical chemical route. The complexity of these analysis and the interest of getting information about the structural profiles of the films have required the use of Grazing-incidence X-ray diffraction (GIXRD) with synchrotron radiation. New insights on the peculiarities of the crystalline characteristics of polycrystalline BNBT thin films arise from the discussion of the results of this work.

2. Experimental procedure

Details of the synthesis for $(\text{Bi}_{0.50}\text{Na}_{0.50})_{1-x}\text{Ba}_x\text{TiO}_3$ precursor solutions can be found elsewhere [22,26]. It can be summarized as follows: $(\text{Bi}_{0.50}\text{Na}_{0.50})_{1-x}\text{Ba}_x\text{TiO}_3$ precursor solutions were synthesized by a hybrid route. Solutions with the stoichiometric nominal compositions and different Ba(II) contents ($x=0.035, 0.055$ and 0.100) were prepared; they are denoted as BNBT3.5, BNBT5.5

and BNBT10.0, respectively. Similarly, $(\text{Bi}_{0.55}\text{Na}_{0.55})_{1-x}\text{Ba}_x\text{TiO}_{3.30}$ nominal solutions containing a 10 mol% excess of Na(I) and a 10 mol% excess of Bi(III), and with different concentrations of Ba(II) ($x=0.055, 0.100, 0.150$), hereinafter BNBTxs5.5, BNBTxs10.0 and BNBTxs15.0, were also synthesized.

Diluted solutions (0.20 M) in dried ethanol were deposited onto Pt/TiO₂/SiO₂/(100)Si substrates (Radiant Technologies) by spin coating at 2000 rpm for 45 s and dried at 350 °C for 60 s, in a hot plate. The as-deposited amorphous films were crystallized by rapid thermal processing (RTP, JetStar 100T JIPELEC) in an oxygen atmosphere at 650 °C for 60 s (heating rate of 30 °C s⁻¹). Deposition, drying and crystallization were repeated six times. Compositions of the $(\text{Bi}_{0.50}\text{Na}_{0.50})_{1-x}\text{Ba}_x\text{TiO}_3$ films were selected (i) for x values lower than the MPB region; (ii) for x values inside the MPB region, and (iii) for x values higher than the MPB region; that means $x=0.035, 0.050$ and 0.100 for BNBT films and $x=0.055, 0.100$ and 0.150 for BNBTxs films [19,26].

In addition to BNBT stoichiometric and BNBTxs thin films, containing 10 mol% excess of Na(I) and Bi(III), BNBT stoichiometric bulk ceramics were studied. For the preparation of bulk ceramics which are taken as a reference, the same solutions with the stoichiometric nominal compositions for $x=0.035, 0.055$ and 0.100 were used. Significant losses of volatiles elements are not expected during annealing of bulk ceramics, therefore Na(I) and Bi(III) excesses were not used here [17,18]. The solutions were dried at 120 °C for 12 h in air. The gels were heated at 350 °C in air for 12 h and subsequently annealed at 800 °C for 2 h (heating rate 2 °C min⁻¹). The powders were mixed with 2-propanol ((CH₃)₂CHOH, Aldrich, 99.5%) used as a binder, and were pressed into discs of 10 mm of diameter and 2 mm of thickness. The green ceramics were sintered in air at 1100 °C for 2 h (heating rate 2 °C min⁻¹). The bulk density of the resulting ceramics were determined by the Archimedes method. The calculated values were 5.62 g cm⁻³ (densification of 94.9%), 5.83 g cm⁻³ (densification of 98.5%) and 5.72 g cm⁻³ (densification of 96.6%) for the BNBT3.5, BNBT5.5 and BNBT10.0 bulk ceramics, respectively.

Rutherford Backscattering Spectroscopy (RBS) experiments were performed to analyze the compositional depth profile of the films. A 5 MV HVEE Tandemron accelerator was used with a 2 MeV He⁺ beam. The data were acquired with a silicon surface barrier detector located at a scattering angle of 170°, with an energy resolution of 16 keV at an ion dose of 10 μC. The experimental spectra were fitted with the software RBS [27].

Plan-view and cross-section micrographs of the crystalline oxide films were obtained by field-emission gun scanning electron microscopy (FEG-SEM, Nova Nanosem 230 FEI Company equipment, Hillsboro, OR).

The crystalline phases were initially studied using a Siemens D500 powder diffractometer with a Cu anode and a Bragg–Brentano geometry. Diffraction patterns of the bulk ceramics were measured in the 2θ interval between 20° and 50°, with a step of 0.05° per each 3 s. More detailed patterns were recorded in the 2θ intervals between 37.0–42.0° and 46.0–47.5°, using a step of 0.005° per each 5 s. These patterns were analyzed with the V1–40 program. Peaks of the patterns were separated and fitted to pseudo-Voigt 2 functions.

The crystalline structure developed in the films was studied using a four-circle diffractometer equipped with a closed Eulerian goniometer (χ, ϕ), a Cu anode, a 120° curve linear position-sensitive detector (CPS120 from INEL SA) and a flat graphite primary monochromator. XRD patterns of 120° in 2θ were recorded in a regular grid of 5° × 5° in χ and ϕ , with χ from 0° to 50° and ϕ from 0° to 355° (a total of 864 patterns). Rietveld refinement calculations were carried out with the Materials Analysis Using Diffraction Package (MAUD) [28]. The refinements were performed on the patterns resulting from the sum of the collected ones for each angular position (χ, ϕ), in order to analyze a randomized

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