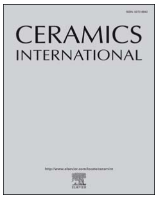
ARTICLE IN PRESS

Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

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



Dielectric, ferroelectric and piezoelectric properties of (1-x)($Bi_{0.5}Na_{0.5})_{0.935}Ba_{0.065}$Ti -$x$($LiSbO_3$) solid solutions

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ARTICLE INFO

Keywords:
Lead-free
Piezoceramics
Ferroelectrics
Dielectrics
Strain
Polarization

ABSTRACT

Compositions in the solid solution series (1-x)($Bi_{0.5}Na_{0.5})_{0.935}Ba_{0.065}$Ti–x($LiSbO_3$), (BNBT-LS) (x = 0, 0.01, 0.02, 0.03, 0.04) have been fabricated via solid state reaction route. Room temperature x-ray diffraction traces of all samples were found to reveal coexistence of the two structures; rhombohedral and tetragonal. The micrographs recorded from the Field Emission Scanning Electron Microscope, provided an overall dense and single phase microstructure for the systems. The dielectric anomalies corresponding to the maximum relative dielectric constant, ε_r, persistently broadened and shifted to low temperatures as a function of increase in $LiSbO_3$ (LS) content. The ferroelectric P − E loops became steadily narrow with similar LS modification showing a continual decline in remnant polarization (P_r) and coercive field (E_c). These phenomena clearly indicated the onset of a growing relaxor-like behavior. The maximum normalized unipolar strain ($S_{max}/E_{max} = d_{33}^* = 400$ pm/V) under the field 50 kV/cm was recorded for the system with x = 0.02.

1. Introduction

Lead-based materials such as Lead Zirconate Titanate, $Pb(Zr_xTi_{1-x})O_3$ (PZT), and PZT-based systems have been extensively used in many piezoelectric devices owing to their excellent properties near the Morphotropic Phase Boundary (MPB). Nevertheless, lead-containing materials have seriously caused lead pollution, health and environmental issues due to the toxic nature of lead oxide [1,2]. Researchers around the world are, therefore, struggling to fabricate Pb-free alternatives that are not only environment friendly but also have a high curie temperature (T_c) [3–7].

Some of the promising lead free materials are the ones with Bismuth Sodium Titanate $(Bi_{0.5}Na_{0.5})TiO_3$, BNT, as a parent/base material. BNT adopts a room temperature rhombohedral structure and shows ferroelectricity with high P_r (38 μC/cm^2). However, the problem with BNT is its hard polling due to the high coercive field ($E_c \approx 73$ kV/cm) resulting in degraded piezoelectric properties and hence, in the first instance, shows no suitability for practical applications [8]. BNT was, therefore, modified on the A- and/or B-site by $BaTiO_3$, La_2O_3, Nb_2O_5 etc. in order to minimize the coercive field and improve the piezoelectric response [3,4]. Amongst these modified systems, $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$ (BNBT6) has attracted great attention because of its classic piezoelectric properties and the existence of Rhombohedral-Tetragonal MPB [9–11]. It has also been reported by Takenaka [12] that near the MPB, $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$ has shown optimized electromechanical properties such as the piezoelectric constants, $d_{33} = 125 \frac{pC}{N}$, $d_{31} = 40 \frac{pC}{N}$, and the coupling factors, $k_{33} = 0.55$, $k_{31} = 0.19$ [13]. N.B. at the MPB, the electric domain wall can turn on easily which may greatly increase the remnant and spontaneous polarizations and thus improves piezoelectric properties [14–17]. Based on the MPB composition, BNBT has also been modified to obtain a large Electric Field-Induced Strain (EFIS) behavior when doped with a new component such as $BiAlO_3$ [18], $Al_6Bi_2O_{12}$ [19], $BaSrTiO_3$ [20] and $K_{12}Na_{12}NbO_3$ [21]. The additions of these new components are likely to manipulate the piezoelectric and EFIS properties of lead-free BNBT systems. EFIS is one of the most important parameters for electromechanical actuators and sensors. BNT-based materials are, therefore, expected to act as potential lead-free candidates.

$LiSbO_3$-doped $(Bi_{0.5}Na_{0.5}K)TiO_3$ (BNKT) systems, for instance, were investigated [22] for high electromechanical properties. $LiSbO_3$ was

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http://dx.doi.org/10.1016/j.ceramint.2017.09.211
Received 30 July 2017; Received in revised form 11 September 2017; Accepted 26 September 2017
0272-8842/

Please cite this article as: Ullah, M., Ceramics International (2017), http://dx.doi.org/10.1016/j.ceramint.2017.09.211

also doped in $(K_{0.5}Na_{0.5})NbO_3$ (KNN) which revealed excellent piezoelectric properties and high curie temperature T_c [22–26] e.g. the work of Zhang *et al.* on $0.948(K_{0.5}Na_{0.5}NbO_3)–0.052(LiSbO_3)$ (KNNLS) has reported [27] the values: $d_{33} \approx 265$ pC/N and $T_c \approx 368$ °C.

To the best of author's knowledge, $LiSbO_3$-doped BNBT systems have not been studied so far. In view of its importance, $LiSbO_3$ have been incorporated in $(Bi_{0.5}Na_{0.5})_{0.935}Ba_{0.065}TiO_3$ at the MPB position. To cut it short, the rationale of the present work is two pronged; (i) synthesis and sintering of $(1\text{-}x)(Bi_{0.5}Na_{0.5})_{0.935}Ba_{0.065}Ti$ $-xLiSbO_3$ (BNBT-LS) ($x = 0, 0.01, 0.02, 0.03, 0.04$) through Solid State Reaction Route (SSRR) and (ii) their electrical (dielectric, piezoelectric, ferroelectric) characterization.

2. Experimental procedures

Ceramic samples of BNBT-LS systems were prepared from reagent-grade raw materials Sb_2O_5 (99.9% Cerac Specialty In-organics, USA), $BaCO_3$ (99.9% Cerac Specialty In-organics, USA), Bi_2O_3 (98.0%), Na_2CO_3 (98.0%), Li_2CO_3(98.0%) and TiO_2 (99.9% High Purity Chemicals, Japan). The dried (at 100 °C for 6 h) and stoichiometrically batched powders were ball-milled for 24 h in ethanol using alumina stabilized zirconia media. The milled slurries were sieved, dried, hand milled and calcined (850 °C for 2 h) in closed crucibles. The reacted powders were remilled similar to the first, followed by hand milling using mortar and pestle. The powders were then moistened with aqueous Polyvinyl Alcohol (PVA) solution to avoid possible latent lateral cracks during pelletization. The powders were uniaxially pressed into disks of 8 mm diameter and 1 mm thickness at a pressure of 100 MPa. Following burnout of the binder at 500 °C, pellets were sintered at 1150–1180 °C (2 h) in the closed alumina segabox. The pellets were covered in powders of their respective compositions to prevent vaporization of elements Bi, Ba, Li, Sb and Na. Light green and dense ceramics of best quality were obtained suitable for further characterization.

Preliminary Phase identification and structural analysis of the reacted powders were carried out by using X-ray diffractometer XRD, X' Pert-PRO MRD, Philips, KBSI. XRD traces were analyzed by using software PDF4$^+$ version 2010. Field-Emission Scanning Electron Microscope (FE-SEM, Hitachi S-4200 & Japan) was employed to examine surface morphology of as-sintered, as-polished and thermally etched (1050 °C for 30 min) samples. Both surfaces of pellets were silver-pasted that functioned as electrodes and were fired (700 °C for 30 min). The Sawyer–Tower circuit with an alternating electric-field having a sinusoidal waveform was applied for measuring the room temperature ferroelectric hysteresis loops of the samples submersed in silicon oil during testing. The electric-field-induced strain (at room temperature) was measured using a Linear Variable Differential Transducer (LVDT, Mitutoyo MCH-331 & M401).

An electric field of 30–40 kV/cm for 30 min was applied for polling the samples in silicon oil. Dielectric data of the samples were acquired using an impedance analyzer model HP4192A as a function of temperature at frequencies 1 kHz, 10 kHz, 100 kHz. Piezoelectric data were recorded via quasi-static method using d_{33}-meter Model ZJ-68.

3. Results and discussion

3.1. Phase assemblage and bulk microstructure

Fig. 1 displays room temperature x-ray diffraction traces taken from the reacted powders of $(1\text{-}x)(Bi_{0.5}Na_{0.5})_{0.935}Ba_{0.065}Ti$ $-xLiSbO_3$ (BNBT-LS) ceramics. No evidence of second phase was observed.

Perovskite peaks for all the compositions were indexed (Joint Committee on Powder Diffraction Standards, JCPDS, Card No 04-012-5546), in the first instance, according to the rhombohedral structure with *R*3*c* (161) symmetry, consistent with the previous reports [4,28]. The rhombohedral (*R*3*c*) distortion was additionally supported by demerging of (111) Bragg's reflection at $2\theta = \sim 40°$ into (003) and (021) peaks. Whereas the parting of reflections (002) and (200) at $2\theta = 46–47°$ points to the existence of tetragonal (*P*4/*m*) structure [29]. There is thus biphasic co-occurrence, rhombohedral and tetragonal.

X-ray diffraction studies produce data that are discernable from the average domains/grains of bulk materials. This technique cannot distinguish between average and local structure e.g dynamics of subtle ion shifting inside a unit cell. XRD spectra, for instance has been reported [30] to give same profile of peaks for both *R*3*c* and $R\,\bar{3}\,c$ space groups that are sequentially ferroelectric and paraelectric versions of rhombohedral structure. We believe that this might be the case with tetragonal centrosymmetric (*P*4/*mbm*) and non-centrosymmetric (*P*4/*m*) versions.

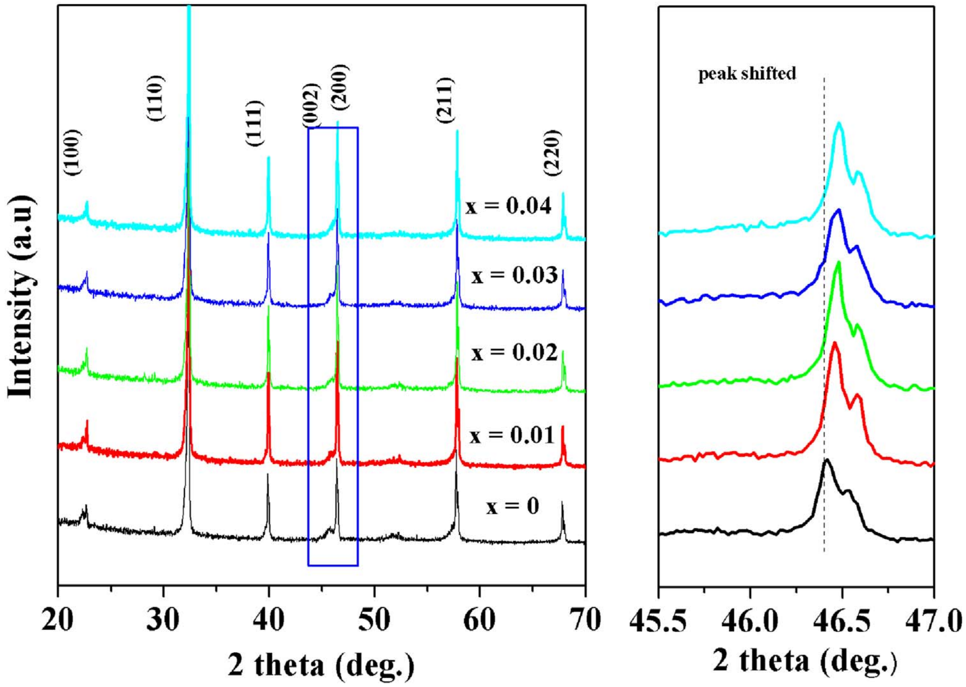

Fig. 1. Room temperature XRD traces of BNBT-LS ceramics.