



Synthesis and characterization of bismuth alkaline titanate powders

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ABSTRACT

In this work, samples of bismuth alkaline titanate, $(K_{0.5}Na_{0.5})_{(2-x/2)}Bi_{(x/6)}TiO_3$, ($x=0.05-0.75$) have been prepared by conventional ceramic technique and molten salts. Metal oxides or carbonates powders were used as starting raw materials. The crystalline phase of the synthesized powders was identified by the X-ray diffraction (XRD) and particle morphology was characterized by scanning electron microscopy (SEM). Solid state reaction method was unsuccessful to obtain pellets. From XRD results, a rhombohedral structure was detected and the parameter lattice were estimated to be $a=5.5478 \text{ \AA}$ and $\alpha=59.48^\circ$. These parameters were used to refine the structure by Rietveld analysis. SEM results showed several morphologies. Apparently, bismuth is promoting the grain growth whose sizes vary from 30 nm to 180 nm. It is expected that these materials can be utilized in practical applications as substitutes for lead zirconatetitanate (PZT)-based ceramics.

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1. Introduction

Since the discovery of the excellent piezoelectric properties of lead zirconate titanate ($Pb(Zr, Ti)O_3$, PZT) at a morphotropic phase boundary (MPB) composition, considerable work has been focused on the development of related lead-based piezoelectric, ferroelectric ceramics and their adaptation to several types of devices as piezoelectric actuators, sensors and transducers [1]. However, the toxicity of lead oxide (PbO) and its vapor pressure during processing, that not only causes environmental pollution but also generate instability of composition and electrical properties of products, have led to a demand for alternative lead-free piezoelectric materials [1]. Nowadays, bismuth-based compositions are widely considered as nontoxic substitutes for piezoelectric materials based on lead. Indeed, Bi^{3+} and Pb^{2+} possess the same lone-pair electronic configurations and a majority of the Bi-containing oxygen octahedral compounds are known to demonstrate ferroelectric properties. At the same time, because of the smaller size of Bi^{3+} as the A-site cation, only a few of the possible bismuth-based perovskite compositions could be obtained by conventional methods at normal pressure [2]. Bismuth sodium titanate, $Bi_{0.5}Na_{0.5}TiO_3$

(abbreviated as BNT), discovered by Smolenskii, in 1960, is one of the important ferroelectrics with perovskite structure and most investigations have been concentrated on the modifications of BNT for applications such as piezoelectric and pyroelectric devices [3], also this material is considered to be a good candidate for a high temperature relaxor as Zhou and Liu mentioned [4]. Nevertheless, BNT has a drawback of high conductivity and high coercive field E_c which cause problems in polarizing process. $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$, as one kind of lead-free BNT ceramics, has been reported to be a promising system [5]. Among the methods to obtain dense ceramics is the molten salts, which provides a simple way to synthesize ceramic powders and is often used to fabricate powders with anisotropic morphology [6].

Therefore, in this work, samples of alkaline bismuth titanate $(K_{0.5}Na_{0.5})_{(2-x/2)}Bi_{(x/6)}TiO_3$, ($x=0.05-0.75$) have been proposed and prepared by a conventional ceramic technique and molten salts in order to determine the effect of the synthesis method on the microstructure. It is expected that these materials can be utilized in practical applications as substitutes for lead zirconatetitanate (PZT)-based ceramics.

2. Experimental procedure

$(K_{0.5}Na_{0.5})_{(2-x/2)}Bi_{(x/6)}TiO_3$, ($x=0.05-0.75$) ceramics were made by conventional solid state reactions and molten salts using high-purity (99.9%) powders of Na_2CO_3 , K_2CO_3 , Bi_2O_3 and TiO_2 . The powders were weighed out to give the desired chemical

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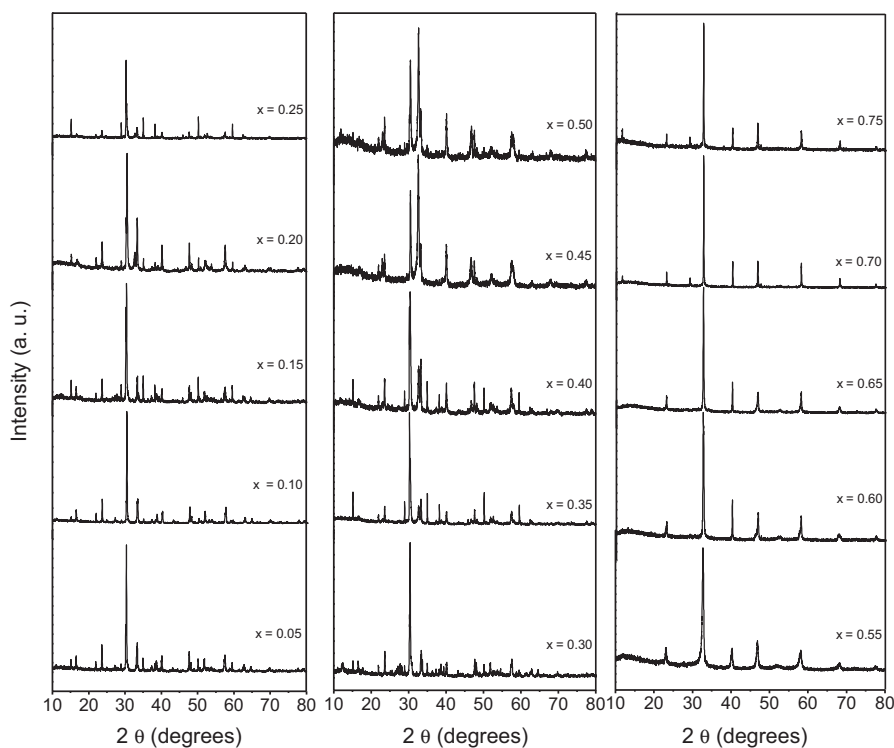


Fig. 1. $(K_{0.5}Na_{0.5})_{2-x/2}Bi_{(x/6)}TiO_3$, $0.05 \leq x \leq 0.75$, diffractograms (solid state reaction).

compositions and hand-milled using acetone as solvent. The mixtures were calcined at 700 °C for 3 h, then hand-milled again in acetone, an attempt to press them and make pellets was done but failed; then, the powders were treated at 800 °C for 3 h. For molten salt method, equimolar NaCl and KCl (Sigma–Aldrich 99.0% purity), used as medium reaction, were mixed and ground homogeneously in an agate mortar. Then, the starting materials and the medium reaction were mixed in a weight ratio of 1:2, and the heat treatment was carried out in closed alumina crucible at 700 °C for 3 h. The powders were washed several times with deionized water to remove the residual salt, and dried in air at 150 °C; then, the dried powders were once again grounded in an agate mortar and pressed at 3.9 MPa and sintering at 800 °C for 3 h.

Structural characterization of the prepared samples was carried out using X-ray powder diffraction (XRD, Bruker AXS Advance D8) with CuK α radiation at 35 kV and 25 mA. Grain sizes were determined by Scherrer equation. Data were collected at room temperature in the 2θ range of 10–80° with a step size of 0.02° and a count time of 1.5 s/step. The unit cell of the crystal lattice was refined, based on XRD data, using Rietveld analysis [7]. Scanning Electron Microscopy (SEM, JEOL JSM-6300) was used in order to study the morphology of the as-synthesized powders, the acceleration voltage was 15.0 kV at 200 \times , 2000 \times and 5000 \times .

3. Results and discussion

3.1. X-ray diffraction (XRD)

Figs. 1 and 2 show the XRD spectra of samples synthesized by solid state reaction. Since the samples with a composition between $0.55 \leq x \leq 0.75$ seem to be one phase, it was decided to work only with these compositions and produce the same solid solutions by molten salts (Fig. 3).

The grain sizes were obtained using the Scherrer equation:

$$t = \frac{k\lambda}{B \cos \theta_B} \quad (1)$$

where t = grain size, λ = X-ray wavelength (Cu K α , 1.5405 Å), B = FWHM, full width at half maximum, θ = Bragg angle, k = constant.

The constant k normally has a value of 0.9 but strictly speaking, this is valid only when the particles are spherical, belong to the cubic system, and are uniform in size; however, the shape and size distributions in a specimen are usually not known; in practice, when the shape is not known, a value of 1.15 is recommended [8].

Then, because the shape has not been determined yet, $k=1.15$ was used to calculate the grain size based on (110) and (214) reflections which are shown in Fig. 4. A similar trend was observed in both solid state reaction and from molten salts, except for (110) signal at $x=0.70$ in the latter method; the grain size increases as bismuth content increases up to a maximum grain size is achieved. Particularly, greater grain sizes are obtained by molten salts than those by solid state reaction. The grain sizes differ for (110) and (214) reflections as a result of the Scherrer equation precision which is more accurate at greater angles; also, Bi³⁺ could be promoted the grain growth up to $x=0.70$ (bismuth content = 0.12), and then, this growth is inhibited.

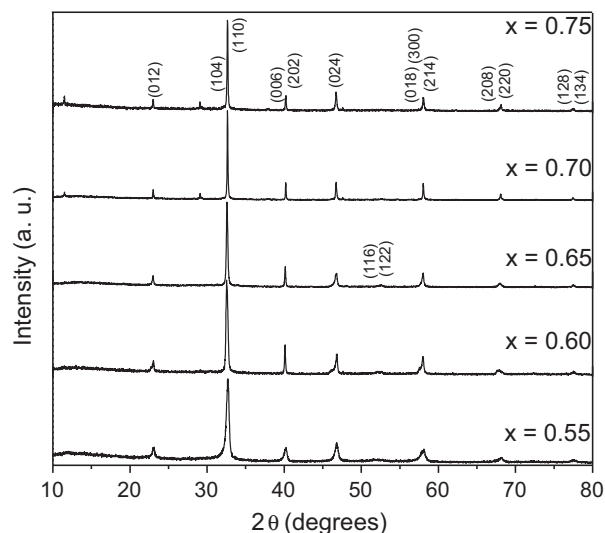


Fig. 2. $(K_{0.5}Na_{0.5})_{2-x/2}Bi_{(x/6)}TiO_3$, $0.55 \leq x \leq 0.75$, diffractograms (solid state reaction).

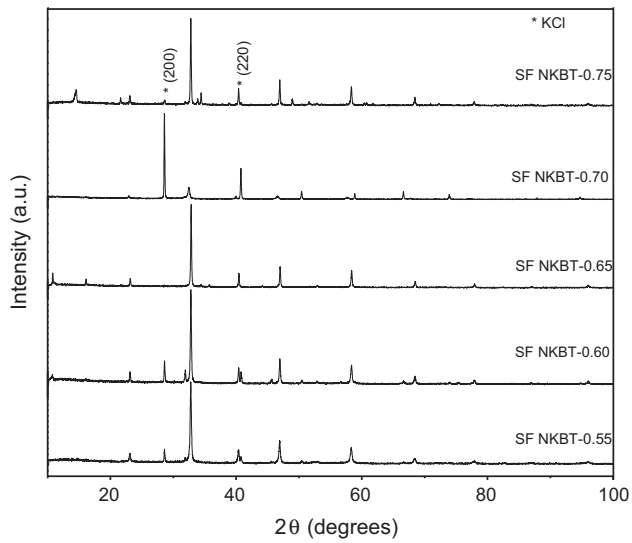


Fig. 3. $(K_{0.5}Na_{0.5})_{(2-x)/2}Bi_{(x/6)}TiO_3$, $0.55 \leq x \leq 0.75$, diffractograms (molten salts).

In order to determine the structure, UnitCell program was used [9]. A rhombohedral structure was supposed and the lattice parameters were estimated: $a = 5.5478 \text{ \AA}$ and $\alpha = 59.48^\circ$ ($a = 5.5046 \text{ \AA}$ and $c = 13.6421 \text{ \AA}$, for hexagonal system). These results are useful as

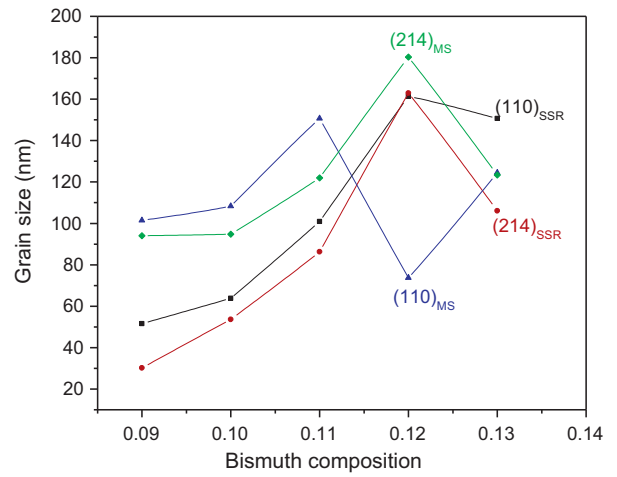


Fig. 4. Bismuth content vs Grain size for molten salts (MS) and solid state reaction (SSR) methods.

starting values for Rietveld analysis. From the Rietveld analysis, it can be said that, even though some changes are observed through the diffractograms, the structure were the same in all the cases ($0.55 \leq x \leq 0.75$) and the lattice parameters did not change (Table 1, maybe because the ionic radii of bismuth and sodium are very

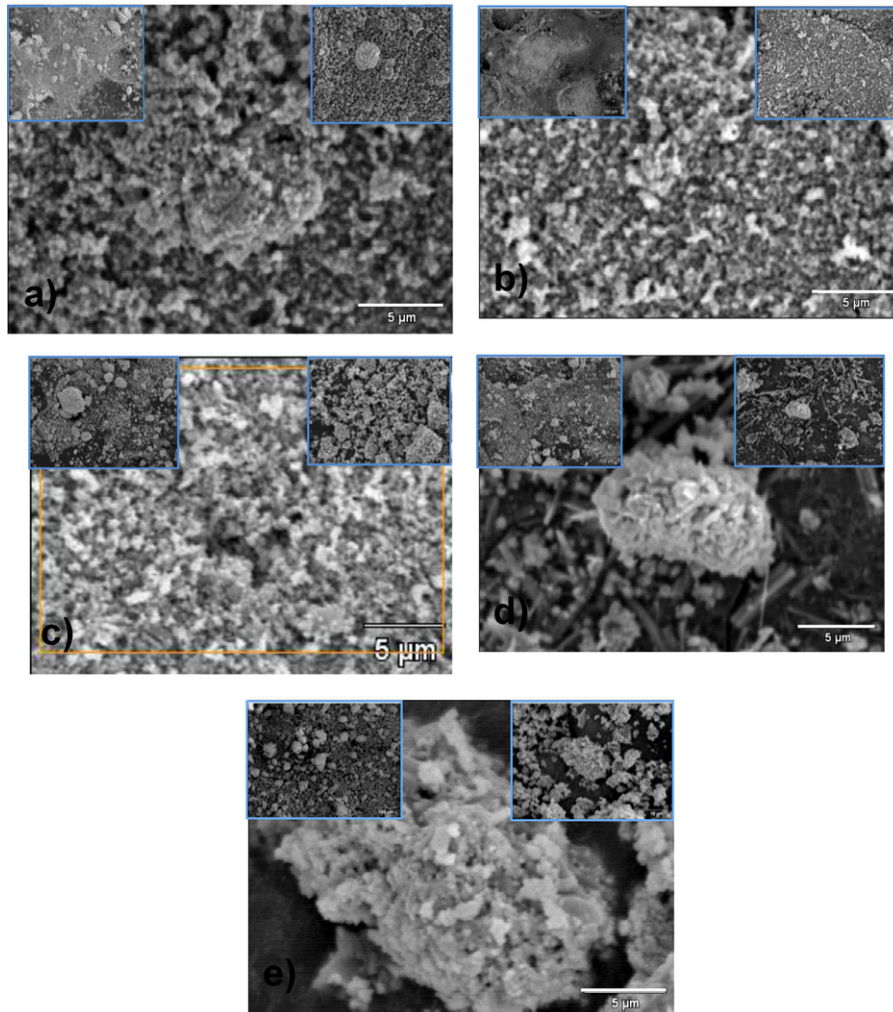


Fig. 5. SEM images of $(K_{0.5}Na_{0.5})_{(2-x)/2}Bi_{(x/6)}TiO_3$ by solid state reaction (a) $x = 0.55$, (b) $x = 0.60$, (c) $x = 0.65$, (d) $x = 0.70$, (e) $x = 0.75$.

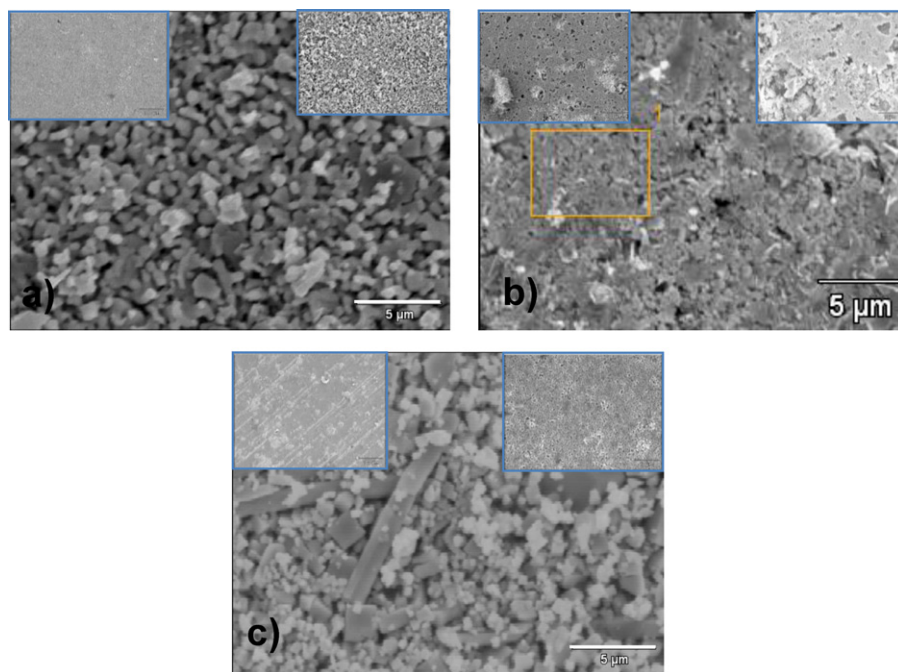


Fig. 6. SEM images of $(K_{0.5}Na_{0.5})_{(2-x/2)}Bi_{(x/6)}TiO_3$ by molten salts (a) $x=0.60$, (b) $x=0.65$, (c) $x=0.70$.

Table 1

Rietveld refinement details for $(K_{0.5}Na_{0.5})_{(2-x/2)}Bi_{(x/6)}TiO_3$ ($0.55 \leq x \leq 0.75$).

R_{wp}	25.07
R_{Bragg}	54.944
R_{exp}	11.51
χ^2	2.18
2θ range ($^\circ$)	3–80
Reflections	25
Spatial group	$R3c$
a (\AA)	5.5257
c (\AA)	13.5800
Volume (\AA^3)	359.0914

close ($r_{Bi^{3+}} = 117$ pm, $r_{Na^+} = 116$ pm) [10] and it could indicate that bismuth occupies sodium sites; however, these results have to be improved due to the R 's and χ^2 values are high. Because of one necessary condition to piezoelectricity in compounds is that the structure has to be non-center symmetric [11], the materials synthesized in this work satisfy this condition: all the samples were rhombohedral (spatial group $R3c$) and the atomic positions are listed in Table 2

3.2. Scanning electron microscopy (SEM)

The electrical properties of polycrystalline ceramics are determined not only by the composition but also by the microstructure, the control of microstructure with grain orientation is very important to obtain ceramics with better performances [12], a SEM study

Table 2

Atomic positions for $(K_{0.5}Na_{0.5})_{(2-x/2)}Bi_{(x/6)}TiO_3$.

	x/a	y/b	z/c
Na	0.00000	0.00000	0.00000
K	0.00000	0.00000	0.00000
Bi	0.00000	0.00000	0.00000
Ti	0.50000	0.50000	0.48200
O (1)	0.00000	0.30000	0.01600
O (2)	0.50000	0.20000	0.51500

was conducted in order to determine the microstructure and morphology of the samples.

Fig. 5 shows the micrographs of the samples $(K_{0.5}Na_{0.5})_{(2-x/2)}Bi_{(x/6)}TiO_3$ ($0.55 \leq x \leq 0.75$) obtained by solid state reaction and Fig. 6 ($0.60 \leq x \leq 0.70$), those obtained by molten salts. From these images, it can be stated that the method used to obtain the solid compounds influenced on the grain size, shape and sinterability. The major drawback with samples from solid state reaction is the difficulty of obtaining high density by the conventional sintering.

An attempt was made to obtain pellets from solid state reaction powders but showed a poor sinterability; then, only powders were obtained which are regular (Fig. 5a–c and e), except for $x=0.70$ (Fig. 5d) where two morphologies are distinguished: one showing elongated grains with a large aspect ratio and another exhibiting non-uniform growth.

Fig. 6a ($x=0.60$) shows regular grains with porous while in Fig. 6b ($x=0.65$) the material is more compact and irregular shapes can be observed. However, on Fig. 6c, regular elongated grains are observed along with some KCl grains arising from the equimolar mixture of NaCl + KCl used in molten salts. The differences among the grain morphology could be the result of the formation of a liquid phase in the Na-excess specimen, as Motohashi and Kimura [13] mentioned that excess Na forms the grains with flat grain boundaries, whereas the grains formed in the stoichiometric and Na-deficient samples show an irregular shape.

4. Conclusions

As bismuth content increases (up to 0.12), the grain size increases up to a maximum grain size is achieved: 160 nm and 180 nm for solid state reaction and molten salts, respectively. In general, the molten salts method produces grains coarser than those obtained by solid state reaction as a result of Na excess. The grain sizes vary from 30 nm to 180 nm, giving a spread of values of 150 nm. The method used to obtain the powders influenced on the grain size, shape and sinterability. An optimization is required in order to ensure and achieve only monophasic compounds. It was

determined that the synthesized materials presented a rhombohedral structure (spatial group $R3c$) which is a necessary condition for the compounds could be piezoelectric properties.

It is expected that the small and homogenous powders influence to lower sintering temperature and to improve piezoelectric properties.

Acknowledgments

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