



Crystal structure refinement of co-doped $\text{Ba}_{0.88}\text{Ca}_{0.12}\text{Ti}_{0.975}\text{Sn}_{0.025}\text{O}_3$ ceramic



Umaru Ahmadu^{a,*}, Oyeleke I. Olarinoye^a, Moses Agida^a, Auwal M. Muhammad^b, Abdulwaliyu B. Usman^a

^a Department of Physics, Federal University of Technology, P.M.B., 65, Minna, Nigeria

^b Centre for Energy Research and Training (CERT), Ahmadu Bello University, Zaria, Nigeria

HIGHLIGHTS

- The crystal structure of BCST is pseudocubic based on Rietveld refinement.
- The structure of BCST evolved from pseudocubic to distorted tetragonal with increasing neutron irradiation.
- Complete displacement Ca^{2+} was observed at maximum irradiation but without oxygen vacancies.
- $\text{Ti}(z)$ position changed with increase in irradiation and this an effect ferroelectricity and dielectric constant.
- The material is expected to suffer some degradation in performance.

ARTICLE INFO

Article history:

Received 6 March 2017

Received in revised form

27 April 2017

Accepted 29 April 2017

Available online 3 May 2017

Keywords:

Ca/Sn-doped barium titanate

Neutron irradiation

Crystallographic parameters

Vacancies

ABSTRACT

Ba/Ca-doped barium titanate has been prepared by solid state reaction to produce $\text{Ba}_{0.88}\text{Ca}_{0.12}\text{Ti}_{0.975}\text{Sn}_{0.025}\text{O}_3$ (BCST) ceramics. Five samples were irradiated using neutron fluence of 8.1×10^6 , 9.72×10^7 , 8.75×10^8 , 6.99×10^9 and 1.4×10^{10} n/cm² (BCST-06 to -10). The structure and phase compositions of the control (BCST) and irradiated samples were determined by X-ray diffraction and indicate the presence of a majorly single phase tetragonal barium titanate (S.G. $P4mm$) with a minor phase CaTiO_3 (orthorhombic). However, Rietveld refinement using GSAS II suite of programs indicates a tetragonality ratio ($c/a = 0.996$) which is pseudocubic with a reduction in volume of 0.03% in the control compared to pristine BT. The irradiated samples exhibited changes in tetragonality (maximum of 0.82%) and variation in volume (0.58%, maximum) over the range of fluence investigated. A complete vacancy was observed in the Ca site of BCST10 but not in the oxygen sites while the occupancies of other metal sites varied. The substitution of Sn is expected to lead to a lower transition temperature and an increase in dielectric constant near the transition temperature of the control. While the changes in volume, tetragonality and occupancy of the irradiated samples are expected to affect their electromechanical properties due to changes in the Ti octahedra which would lead to a slight degradation in device performance.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Barium Titanate (BT) with Perovskite crystal structure (ABO_3) has many industrial, technological and scientific importance, due to its superior dielectric, ferroelectric and piezoelectric properties. At high temperature BT has a paraelectric cubic structure and changes to a ferroelectric tetragonal type structure at 393–403 K which has

high dielectric constant near the temperature of ferroelectric–paraelectric transition known as the Curie point (T_C). These transitions could also be brought about by a reduction of the size of the ceramic (nanocrystalline BT, so-called “size effect”), addition of dopants and specifically for this work, by irradiation. Irradiation has the advantage of not only inducing phase transition but introducing point defects in the structure which can be used to evaluate degradation of performance of device in neutron environments for instance. BT powders have been synthesized conventionally using solid state reaction at temperatures higher than 1473 K whereas high energy ball-milling with calcinations at 940 °C show weak

* Corresponding author.

E-mail address: u.ahmadu@yahoo.com (U. Ahmadu).

diffraction peaks for Ba_2TiO_4 intermediate phase [1]. Detailed structure, atomic coordinates and properties of BT and dopants have been reported in literature [2–9]. Lead-based piezoelectrics are currently dominant in the market where they are used in sensors, actuators, energy harvesters and transducers, among others [5]. The presence of lead leads to pollution in the environment and necessitates the need for alternatives such as BCTZ (Ba,Ca)(Ti,Zr) O_3 and BCTS (Ba,Ca)(Ti,Sn) O_3 ceramics which have the potential to replace the lead-based ones on account of their high piezoelectric properties [5]. Introduction of various dopants, particularly, isovalent cations at both the A and B sites of BT increases the dielectric constant and reduces the Curie point [2].

Sn-containing titanate ceramics have favourable dielectric properties [6]. Increase of Sn to 15 mol% in BT can lead to the shifting of the paraelectric to ferroelectric phase transition temperature to lower temperature with concomitant increase of dielectric constant [2]. The T_c of BTS is also controlled by adjustment of the Ti/Sn ratio which structurally transforms from centrosymmetric cubic to non-centrosymmetric tetragonal phase at room temperature for $x = 0.12$ (where x is the amount of Sn) [2]. BTS materials are important in the electroceramic industry due to their superior dielectric properties which are useful for practical applications in ceramic capacitors, among others [7]. Studies have been reported on many Sn-doped systems, such as $\text{Ba}_{0.97}\text{Ca}_{0.03}\text{Ti}_{0.96}\text{Sn}_{0.04}\text{O}_3$ [5] and $\text{BaTi}_{0.975}\text{Sn}_{0.025}\text{O}_3$ ($c/a = 1.0063$, volume = 64.42 \AA^3 , S.G., $P4mm$ -tetragonal) systems [2] with mixed outcomes on phase composition, among others. Results on Rietveld refinement of $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ ($0 \leq x \leq 0.2$) ceramics using neutron powder diffraction showed a crystal which is a mixture of $P4mm$ and $Amm2$ (orthorhombic) phases ($0.025 \leq x \leq 0.07$) while other workers [8] on $\text{Ba}_{1-x}\text{Sn}_x\text{O}_3$ ($0.0 \leq x \leq 0.05$) ceramics found a low content of cubic phase infused accompanying Sn doping of BT ceramics (tetragonal phase) and an increase in unit cell volume. However, on further doping with a small amount of Sn ($x \leq 0.03$) it was found to reduce the amount of defects in pristine BT ceramics with a concomitant increase in permittivity. There is therefore a question as to the actual phase admixture in Sn-doped BT based on the concentration of dopant (Sn).

On the other hand, the addition of dopants such as Ca in the Ba site has a different effect due to the very large size of Ba ion which leads to a large octahedral site in BT in which the titanium ions can readily move. Thus, the substitution of isovalent cations such as Ca^{2+} at the Ba site alters the lattice parameters, dielectric properties [7] and reduces the size of the octahedral site, thereby restricting the motion of the Ti ion with a consequent decrease in sensitivity to temperature due broadening of the temperature vs dielectric constant curve [9]. There is also the problem of phase composition for this compound as different phases have been reported depending on composition. The solid solution $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ ($x = 0.05$ to 0.9) shows single phase (up to $x = 0.3$) after which it becomes diphasic. Ca^{2+} is smaller in ionic radius but has greater atomic polarizability which induces the interaction between the T_i ions and compensates for the decrease in T_c observed [7,10]. BT (tetragonal) has bulk unit cell volume of $64.271(4) \text{ \AA}^3$ and c/a ratio of 1.011 [3]. The solid solution $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ ($0.05 \leq x \leq 0.9$) shows the formation of single phase up to $x = 0.3$, whereas it was reported [11] that the thin film system $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ showed distinct tetragonal splitting for lower concentrations of x which eventually merged into a single peak for $x > 0.21$ and led to a cubic phase at room temperature. Additional peaks observed showed a secondary phase of Ca-rich regions (CaTiO_3 , orthorhombic) which grew stronger with higher Ca content. The c/a ratio decreased with increase in Ca content ($x > 0.05$) and shrank in the unit cell volume, while the phase transition temperature and the dielectric constant both decreased with increase in Ca content. Tetragonal and orthorhombic peaks in

$\text{Ba}_{0.70}\text{Ca}_{0.30}\text{TiO}_3$ (BCT) ceramics prepared by solid state reaction corresponding to perovskite BT and CaTiO_3 , respectively, have been reported [12,13]. The tetragonal peaks were found to be isostructural with $\text{Ba}_{0.88}\text{Ca}_{0.12}\text{TiO}_3$ (JCPDS81-1288), i.e., same as the Ca concentration in the current work. Sintering at high temperature ($1500 \text{ }^\circ\text{C}/6 \text{ h}$) eventually reduced the orthorhombic peaks with consequent reduction in the tetragonal distortion ($c/a \sim 0.99$). In all these cases the Curie point (T_c) was found to be nearly temperature independent of the Ca doping concentration but the transition temperatures shifted to lower temperatures [14]. Another problem reported in literature is that of small amount of Ca^{2+} ions which have been observed to substitute for Ti^{4+} ions in $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ (BCT), provided the molar ratio of $(\text{Ba} + \text{Ca})/\text{Ti} \geq 1$. This is reported to lead to some abnormalities in both properties and structure for bulk materials if solid state reaction technique is used [10,12].

When neutron irradiations interact with BT ceramics, there is much to be studied in terms of quantification of the defects they induce, phase transitions and the consequent effect on the ferroelectric and dielectric properties and thus on performance. Neutrons (thermal) are effective in causing impurity production and atomic displacements through the transmutation of nuclei into other nuclei which by themselves may in turn be radioactive. The mechanism is as a result of fission and activation (capture). Atomic displacements occur when atoms are dislodged from their normal positions in the structure of the material. Displaced atoms can leave lattice vacancies and lodge in interstitial locations and may also cause interchange of dissimilar atoms in the lattice structure [15]. Several studies have shown that irradiation with neutrons, causes irreversible changes to electro-mechanical properties. Nuclear irradiations (neutron and gamma) of BT-based ceramics alter the piezoelectric, dielectric, microstructure and structural properties [15–18]. There is very little that is known about the type and concentration of point defects and other structural features produced during irradiation. Reports indicate a decrease in the planar electromechanical coupling factor k_p , increase in unit cell volume and decrease in lattice aspect ratio with increasing irradiation. Irradiation of single crystal BT at $\sim 100 \text{ }^\circ\text{C}$ with fast neutron flux of $1.8 \times 10^{20} \text{ n/cm}^2$ showed the transformation of the tetragonal single crystals to perovskite-type cubic single crystal which are normally stable at $120 \text{ }^\circ\text{C}$ and the lattice parameters exhibited anisotropic expansion [19]. Increase in unit cell volume and decrease in lattice aspect ratio (c/a) with increase in neutron irradiation have been reported in BT [20]. Others [15] have reported structural changes in $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ after exposure to a 1 MeV equivalent neutron fluence of $1.7 \times 10^{15} \text{ neutron/cm}^2$ and ascribed it to increased concentration of oxygen vacancies. The irradiation thresholds of some pressure transducers based on BT have been reported to be $7.6 \times 10^{10} \text{ n/cm}^2$, for bulk damage to occur [21]. Generally, there is scanty literature on the structural and microstructural defect of Sn-doped BT. Though techniques such as positron annihilation lifetime spectroscopy and co-incident Doppler-broadening spectroscopy have been reported in the study of structural defects in Sn-doped BT, but this is an expensive technique compared to Rietveld method, for example.

Recently, however, diffraction has been used to characterize the effect of irradiation on materials which are BT-based [15], since diffraction intensities are a function of the scattering factors of the constituent atoms and their site occupancies. It means that site occupancies are deducible from the diffraction patterns. The Rietveld method is one sure way that provides a quantitative approach to measure and thus model the diffraction patterns in order to deduce quantitative information about lattice parameters, site occupancies, and microstructural information, amongst others. In particular, site occupancies are fundamental in that they are a direct measure of evolving point defect concentrations with increase in

irradiation; whereas, the lattice parameters are an indirect measure of the point defects. Thus application of Rietveld refinement to defect concentration characterisation is novel approach for study of irradiated materials.

In the present work, the crystal structure of the system $\text{Ba}_{0.88}\text{Ca}_{0.12}\text{Ti}_{0.975}\text{Sn}_{0.025}\text{O}_3$ considered as a binary system ($\text{Ba}_{0.88}\text{Ca}_{0.12}\text{TiO}_3$ and $\text{BaTi}_{0.975}\text{Sn}_{0.025}\text{O}_3$) which has the reported features of Ca/Sn-doped BT prepared by solid state reaction has been analysed by the Rietveld method. This composition has not been studied before to our knowledge and it is expected that the combination of suitable physical properties of the component systems would result in enhancement of their physical properties to enable the determination of the phase composition and structural parameters of the system for stability of device in operation. Similarly, the evolution of the structure, with specific reference to defect parameters have been discussed with increasing neutron irradiation using GSASII (General Structure Analysis System II suite of programs) [22] in order to elucidate the problems highlighted above.

2. Experimental procedures

Stoichiometric amounts of the starting materials were used. The details of the preparation and synthesis conditions have been reported in our earlier work [23].

Meanwhile, sintered and pelletized samples were irradiated in a low neutron flux irradiation facility [24] which exists as a 750 mm by 800 mm paraffin cylinder having at its centre a 5 Ci Am-Be isotopic neutron source (diameter 30 mm, and height 48 mm) with average thermal neutron flux of 2.7387×10^4 n/cm².s. There are six irradiation ports arranged symmetrically around the source. These provide opportunity for simultaneous irradiation of six samples at a time. For the purpose of this work, five groups of pellets of the samples were placed in a polythene bag and lowered into the ports with the aid of a thread. The pellets were irradiated at 8.1×10^6 , 9.72×10^7 , 8.75×10^8 , 6.99×10^9 and 1.4×10^{10} neutron fluence. The samples were subsequently labelled BCST-06, BCST-07, BCST-08, BCST-09 and BCST-10, respectively. To attain the required neutron fluence, the pellets were brought out after successive irradiation times of 6 min, 1 h, 9 h, 72 h and 144 h have elapsed. Literature survey showed that BT has a flux threshold of 2.1×10^4 n/cm².s and experiences bulk damage at neutron fluence of 7.6×10^{10} n/cm² [21]. This informed the choice of the neutron fluence used in the present study.

X-ray Diffractometer (D8 Advance, BRUKER AXS, 40 kV, 40 mA) with monochromatic $\text{CuK}\alpha$ ($\lambda = 1.54060$ Å) over a step scan mode of step size 0.034° and counts accumulated for 0.5 s at each step for 2θ values ranging from 20° to 90° was used to characterize the structural phase composition of the pristine and irradiated ceramics.

Rietveld structure refinement was used to model the data. The instrument parameter file was obtained from the default in GSAS II [22] which is generic parameter file for $\text{CuK}\alpha 1+2$ for Bragg-Brentano diffraction geometry with zero correction of -0.07° , POLA of 0.911 and IPOLA was set to 1. Finger Cox Jephcoat (FCJ) peak asymmetry ratios of S/L and H/L defaults value (0.002) was used. Background coefficients with 9 terms and function type log interpolate were used. Different refinement strategies were applied on each sample in order to arrive at a good convergence minimum. Some of the samples had to undergo several trials in order to achieve the desired result. The main strategy adopted was to first refine the structure using default histogram scale factor, while the background was adjusted to log interpolate. Next, the lattice parameters were set to refine by setting the thermals and fractional constraints. The atomic parameters, starting with thermals/

coordinates in the case of O (1) and O (2) and only thermals for the others, were subsequently refined. These were followed by the coordinates for the Ba/Ca and Ti/Sn sites. The U, V and W instrument parameters were then refined, followed by sample parameters (in some cases crystallite size/microstrain were refined). Structural parameters (coordinates, site fraction, and isotropic thermal displacement) were also refined. The site fractions of Ba/Ca and Ti/Sn were refined according to the nominal compositions to unity and were constrained. The thermal displacement parameters were set to be equivalent for Ba/Ca and Ti/Sn. The lattice parameters used and the atomic coordinates were obtained from literature [25,26] with $a = 3.994$, $c = 4.036$, respectively, and were used as the starting values for refinement of the unit cell. The Ideal perovskite structure is cubic with space group $Pm\bar{3}m$. Within a unit cell the A and B sites are crystallographically independent. Tetragonal BT has space group $P4mm$ and the atomic positions are at special Wyckoff sites: the A cation occupies the 1a site (0, 0, 0); the B cation occupies the 1b site (1/2, 1/2, z); atom O1 occupies the 1b site (1/2, 1/2, z) and atom O2 is at the 2c Wyckoff site (1/2, 0, z). Even though these site positions were set to refine they retained their special positions, except the z coordinate which is arbitrary and refinable. Only tetragonal BCST phase was refined in all samples as the small intensity peaks' contribution to the overall refinement, after several trials, were insignificant in the refinement plots and values of the agreement factors.

3. Results and discussion

The X-ray diffraction patterns of the synthesized BCST (control) ceramics and those exposed to different neutron fluence are depicted in Fig. 1. Indexing of the peaks indicate that the control and irradiated samples of BCST ceramics are polycrystalline and compare well with JCPDS No. 00-005-0626 file for tetragonal phase BaTiO_3 . Minor peak with very low intensity at $\sim 47.5^\circ$ (2θ) was observed and identified as orthorhombic phase (JCPDS File No. 00-022-0153). There are unidentified peaks close to the peak of highest intensity and another as indicated in Fig. 1. The tetragonal system has Space Group $P4mm$.

Fig. 2 is a representative plot of the refinement for sample BCST07 where the crosses (+) represent the data points, the continuous lines the fittings (model), the green continuous lines below zero the difference plot and the vertical lines the peak positions. It can be seen that all the major peaks have been indexed according to tetragonal $P4mm$ S.G., while the peak close to 30° 2θ which is due to CaTiO_3 orthorhombic was not refined and had no effect even on application of diphas refinement. The agreement factors (weighted) for the refined sample converged at 10.79, 5.88, 8.55, 9.05, 10.13 and 8.27% for BCST and BCST06-10, respectively, which are reasonable values considering the good fit of the intensities and peak positions for all the samples, except those due to the unknown and CaTiO_3 , and is an indication of a good model.

Visually, the BCST (control) is the one with nearly perfect fit. The unknown peaks were further reduced in intensity in BCST06 and BCST10, in particular, perhaps due to their displacement at the atomic sites and therefore lost their scattering contribution to the pattern. Attempts to do a diphas refinement for the samples using known coordinates of CaTiO_3 [27,28] did not yield significant changes, both visually and based on the agreement factors. The results of the refinement and quality of fit are listed in Table 1 for evaluation. It can be observed that although the control and all the irradiated samples were all indexed based on tetragonal symmetry, their c/a ratios varied.

In order to understand the crystallographic parameters of the refined control ($\text{Ba}_{0.88}\text{Ca}_{0.12}\text{Ti}_{0.975}\text{Sn}_{0.025}\text{O}_3$) and the effect of neutron irradiation on it, one can assess the control from the point

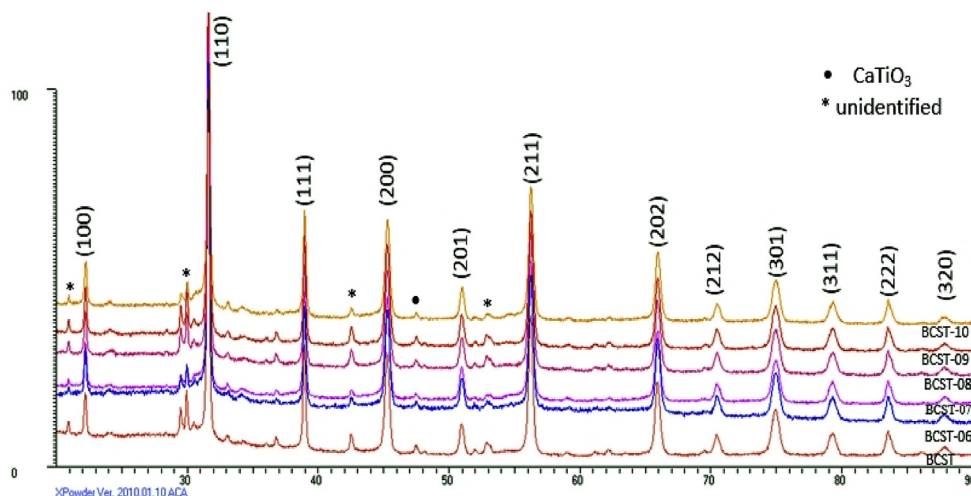


Fig. 1. Composite X-ray diffraction patterns of control (BCST) and irradiated samples. The secondary phase and Miller indices are indicated for the tetragonally indexed system.

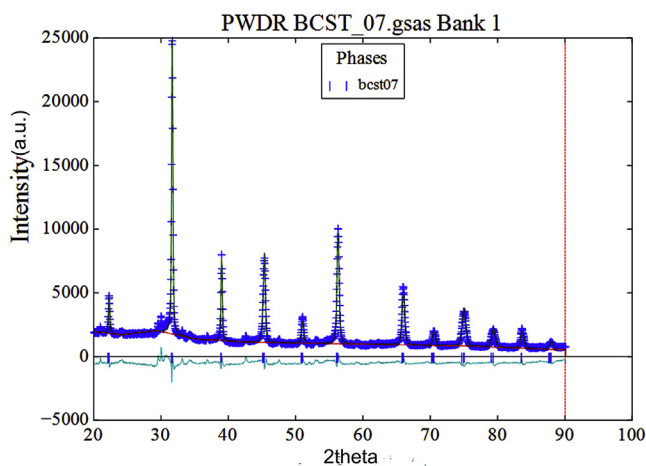


Fig. 2. Representative Rietveld refinement plot of irradiated BCST07 showing a pseudocubic system based on tetragonality ratio. The peak positions and intensities are well-fitted which is an indication of the appropriateness of the model used. The Crosses (+) are the data points, continuous line are the fitting (model), the green continuous line below zero is the difference plot and the vertical lines indicate peak positions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of view of the effect of Ca^{2+} substitution on pristine BT, followed that of Sn to form BCST and then compare the results with those reported in literature. Accordingly, the following specific property changes on the crystallographic and physical properties have been observed within the context of the concentrations studied in order to explain the observed crystallographic properties of (BCST) ($\text{Ba}_{0.88}\text{Ca}_{0.12}\text{Ti}_{0.975}\text{Sn}_{0.025}\text{O}_3$).

The volume of BT pristine was increased by the small amount of Sn dopant ($x = 0.025$) and was subsequently reduced by $\sim 0.03\%$ on co-doping with Ca/Sn, hence the reduction in volume of BCST control to 64.250 \AA^3 as presented in Table 1. Ca substitution decreased the volume of the unit cell while co-substitution with Sn simultaneously increased it [8,11]. In addition, though the structure of the control remained tetragonal, it became highly distorted as reflected in the c/a ratio of 0.996, which is near cubic enough (pseudocubic). The small intensity Ca-rich regions observed indicate that the control is diphasic (orthorhombic/ $Amm2$). Sn doping is known to result in a mixture of $P4/mmm$ and $Amm2$ phases together

with some small infusion of cubic system ($Pm\bar{3}m$) [2,8] for this concentration. On the other hand, Ca doping has been reported to lead to a tetragonal/orthorhombic or single phase tetragonal system up to $x = 0.3$ [11,13]. Attempts to do a sequential refinement with the CaTiO_3 phase failed due to the very few peaks (2) and their very low intensities which are an indication of the dominance of the tetragonal structure. Sn doping has also been observed to reduce the amount of defects in BT and could be an explanation for the lack of oxygen vacancies measured, apart from the level of the maximum radiation fluence used [8]. The control is therefore expected to have a low transition temperature and high dielectric constant at the transition temperature as a result of the co-doping. In the irradiated samples, the phases varied between pseudocubic and distorted tetragonal (0.9946(2) and 1.004(2)) throughout the range of fluence used and imply that irradiation can be used to induce phase transition of a high temperature cubic paraelectric phase of BT (usually obtained at $120\text{--}130^\circ\text{C}$) to room temperature in the case of BCST06/09.

The fractional site occupancies for Ba/Ca reduced considerably compared to the nominal composition to the value of 57:43 in the refined. This ratio however, is approximately equal in BCST07 and BCST08 (51:49 and 48:52, respectively) whereas the ratios are $\sim 87:13$, $81:19$ and $100:0$ in BCST06, BCST09 and BCST10, respectively. The most interesting result is that of BCST10 where the Ca ions have been completely dislodged from their site which is at the maximum irradiation; whereas the Ba ions suffered relatively small displacements. The site occupancy ratios of Ti/Sn shows that Ti is occupying 87:13, 81:19, 83:17, 84:16, 60:40 and 94:6 in BCST, BCST06-10 which is an indication that Ti suffered maximum displacement in BCST09, while Sn was relatively less displaced. However, the fractional occupancies of O(1) and O(2) were unchanged throughout and imply that neutron irradiation did not cause vacancies at these sites, partly due to the level of irradiation used and the inhibition of vacancy formation by Sn doping, a fact that is in sharp contrast with other reports [15] where higher neutron fluence was used. Similarly, though the ratio of Ba + Ca/Ti ≥ 1 , the fact that oxygen vacancies were not observed in the control BCST sample after refinement could be an indication that Ca^{2+} did not substitute the Ti ion sites which would have resulted in vacancies for charge balance [12,13]. Moreover, the site occupancies did not show any stoichiometry problems but the concentration of Ca may be inadequate to project the phenomenon.

With reference to the control (BCST), the changes in volume

Table 1
Lattice parameters, site coordinates tetragonality ratios, agreement/weighted agreement factors and χ square values of control and irradiated BCST ceramics. The values in parenthesis are the estimated standard deviation of the last value calculated from the refinement.

BCST					BCST06				
a (Å)	c (Å)	Cell volume (Å ³)	c/a	Profile fit	a (Å)	c (Å)	Cell volume (Å ³)	c/a	Profile fit
4.010(5)	3.994(6)	64.25(0)	0.996(1)	R _p = 7.40% R _{wp} = 10.78% χ^2 = 15.04	4.008(6)	3.994(2)	64.18(2)	0.9946(2)	R _p = 4.48% R _{wp} = 5.88% χ^2 = 5.44
Site Positions					Site Positions				
x		y	z	Occ.	x		y	z	Occ.
Ba	0.0	0.0	0.00(7)	0.57(8)	Ba	0.0	0.0	-0.01(6)	0.87(6)
Ca	0.0	0.0	0.0(1)	0.43(2)	Ca	0.0	0.0	8.2(1)	0.13(4)
Ti	0.5	0.5	0.50(6)	0.87(4)	Ti	0.5	0.5	0.4(7)	0.81(1)
Sn	0.5	0.5	0.5(3)	0.13(6)	Sn	0.5	0.5	1.4(7)	0.19(9)
O(1)	0.5	0.5	0.0(2)	1	O(1)	0.5	0.5	-0.0(2)	1.0
O(2)	0.5	0.0	0.44(4)	1.0	O(2)	0.5	0.0	0.43(0)	1.0
BCST07					BCST08				
a (Å)	c (Å)	Cell volume (Å ³)	c/a	Profile fit	a (Å)	c (Å)	Cell volume (Å ³)	c/a	Profile fit
3.992(2)	4.008(4)	63.88(4)	1.0039(6)	R _p = 6.55% R _{wp} = 8.55% χ^2 = 11.24	3.996(7)	4.013(6)	64.11(2)	1.004(2)	R _p = 6.30% R _{wp} = 9.05% χ^2 = 12.64
Site Positions					Site Positions				
x		y	z	Occ.	x		y	z	Occ.
Ba	0.0	0.0	0.00(2)	0.51(1)	Ba	0.0	0.0	-0.0(1)	0.48(3)
Ca	0.0	0.0	0.0(1)	0.48(9)	Ca	0.0	0.0	-0.01(6)	0.51(7)
Ti	0.5	0.5	0.50(7)	0.83(3)	Ti	0.5	0.5	0.51(4)	0.84(3)
Sn	0.5	0.5	0.51(4)	0.17(6)	Sn	0.5	0.5	0.51(7)	0.16(7)
O(1)	0.5	0.5	0.0(4)	1.0	O(1)	0.5	0.5	-0.0(2)	1.0
O(2)	0.5	0.00	0.42(9)	1.0	O(2)	0.5	0	0.55(2)	1.0
BCST09					BCST10				
a (Å)	c (Å)	Cell volume (Å ³)	c/a	Profile fit	a (Å)	c (Å)	Cell volume (Å ³)	c/a	Profile fit
4.011(7)	3.995(8)	64.30(9)	0.9961(3)	R _p = 6.88% R _{wp} = 10.13% χ^2 = 16.29	3.999(5)	4.015(0)	64.19(2)	1.0041(3)	R _p = 6.30% R _{wp} = 8.27% χ^2 = 10.94
Site Positions					Site Positions				
x		y	z	Occ.	x		y	z	Occ.
Ba	0.0	0.0	-0.04(3)	0.81(9)	Ba	0.0	0.0	0.06(7)	1.00(4)
Ca	0.0	0.0	0.1(9)	0.19(1)	Ca	0.0	0.0	4.(7)	0.00(4)
Ti	0.5	0.5	0.4(6)	0.6(9)	Ti	0.5	0.5	0.58(3)	0.94(4)
Sn	0.5	0.5	0.4(6)	0.4(1)	Sn	0.5	0.5	2.9(6)	0.05(6)
O(1)	0.5	0.5	-0.0(7)	1.0	O(1)	0.5	0.5	1.0(7)	1.0
O(2)	0.5	0.0	0.4(9)	1.0	O(2)	0.5	0.0	0.52(2)	1.0

observed in the irradiated samples are +0.11%, +0.58%, +0.21%, -0.09% and 0.09%, for BCST06–10, respectively. The volumes initially decreased with increase in irradiation, increased and finally decreased near the irradiation maxima. This is in accordance with the variation of the lattice parameter *a*. However, the variations in the lattice parameters *a/c* are anisotropic as has been reported in literature elsewhere. The changes in lattice aspect ratio observed are in the range 0.036%–0.82% compared with the control sample and these are seen to increase initially, decrease and subsequently increase toward the irradiation maxima in accordance with volume. These changes in unit cell volume and lattice aspect ratio are deemed significant compared to the report by some workers [15].

To ensure consistency in the output of the refinement, the refinement was repeated for all the samples without constraints applied to the Ba/Ca and Ti/Sn sites and the site fractional coordinates for each were made to unity and then refined. Oxygen vacancies were still not observed.

These changes imply that in agreement with literature, neutron irradiation indeed affect electromechanical properties within the limits of the maximum neutron fluence applied and thus make it

sensitive compared to findings on other doped BT ceramics where higher fluence have been used [15,21]. The present work demonstrates that neutron irradiation does not create oxygen vacancies on either sites of O(1)/O(2) and that the occupancies of Ba/Ti generally suffer more displacements, factors which are expected to alter the observable properties of the material. The changes in values of the samples' physical parameters can therefore be deemed significant.

4. Conclusions

Ba_{0.88}Ca_{0.12}Ti_{0.975}Sn_{0.025}O₃(BCST) was synthesized by solid state reaction. Phase analysis showed major phase of tetragonal barium titanate with S.G. *P4mm* and orthorhombic CaTiO₃ (S.G. *Amm2*). Irradiation of the BCST at 8.1×10^6 , 9.72×10^7 , 8.75×10^8 , 6.99×10^9 and 1.4×10^{10} n/cm² (BCST-06 to -10) showed differing structural changes with structural transformation in the ceramic compared to the control. Rietveld refinement of the structure based on GSAS II showed reduced lattice parameters, unit cell volume and tetragonality in the control and a pseudocubic structure at room temperature, whereas the irradiated samples showed variations between the pseudocubic and distorted tetragonal phases.

Variations in the site occupancies of Ca/Sn in particular, were observed but none in the oxygen sites, with complete atomic displacement observed in BCST10 in Ca. There was also no observation of Ca substituting Ti sites as reported, which could be due to the concentration of Ca used. These variations are deemed significant and are expected to affect the electromechanical properties of the BCST in neutron environment. The transition temperature of the BCST is expected to decrease with an increase in the value of the dielectric constant near the paraelectric-ferroelectric phase transition at room temperature. The irradiated samples are therefore expected to show some degradation in performance.

Acknowledgement

This work was funded by the Tertiary Education Trust Fund (TETFUND) under project no: TETFUND/FUTMINNA/2014/044.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.matchemphys.2017.04.063>.

References

- [1] X.M. Chen, Y. Zhang, W.W. Kong, X.B. Bian, J.P. Zhou, P. Liu, J. Ceram. Process. Res. 11 (2010) 475–478.
- [2] L. Veselinovic, M. Mitric, L. Mancic, M. Vukomanovic, B. Hadzic, S. Markovic, D. Uskokovic, J. Appl. Cryst. 47 (2014) 999–1007.
- [3] M.B. Smith, K. Page, T. Siegrist, P.L. Redmond, E.C. Walter, R. Seshadri, L.E. Brus, M.L. Steigerwald, J. Am. Chem. Soc. 130 (2008) 6955–6963.
- [4] S. Pradhan, G.S. Roy, Researcher 5 (2013) 63–67.
- [5] C.-C. Tsai, W.-H. Chao, S.-Y. Chu, C.-S. Hong, C.-M. Weng, H.-H. Su, AIP Adv. 6 (2016) 125024.
- [6] F.I.H. Rhouma, A. Dhahri, J. Belmabrouk, M.A. Valente, Solid State Commun. 152 (2012) 1874–1879.
- [7] A. Moquim, M.R. Panigrahi, Process. Appl. Ceram. 9 (2015) 91–98.
- [8] Z. Liljuan, W.L. Hai, L. Jiandang, C. Bin, Z. Minglei, Y. Bangjiao, J. Phys. Conf. Ser. 443 (2013) 012014.
- [9] K.I. Osman, Synthesis and Characterization of BaTiO₃ Ferroelectric Material, Ph.D Thesis, Cairo University, Egypt, 2011.
- [10] S. Yun, X. Wang, B. Li, D. Xu, Solid State Commun. 142 (2007) 461–465.
- [11] P. Victor, R. Ranjih, S.B. Krupnadh, J. Appl. Phys. 94 (2003) 7702–7709.
- [12] R.K. Zheng, J. Wang, X.G. Tang, Y. Wang, H.L.W. Chan, C.L. Choy, J. Appl. Phys. 98 (2005) 084108.
- [13] V.S. Puli, D.K. Pradhan, B.C. Riggs, D.B. Chrisey, R.S. Katiyar, J. Alloys Compd. 584 (2014) 369–373.
- [14] F. De Shang, I. Mitsuru, Role of Ca Off-centering in Tuning the Ferroelectric Phase Transitions in Ba(Zr,Ti)O₃ System in “Ferroelectrics”, In-Tech Open source publications, 2015.
- [15] A. Henriques, J.T. Graham, S. Landsberger, J.F. Ihlefeld, G.L. Brennecke, D.W. Brown, J.S. Forrester, J.L. Jones, AIP Adv. 4 (2014) 117125.
- [16] I.J. Lefkowitz, J. Phys. Chem. Solids 10 (1958) 169–173.
- [17] N. Medhi, A.K. Nath, J. Mater. Eng. Perform. 22 (2013) 2716–2722.
- [18] A.K. Nath, A. Medhi, Indian J. Phys. 89 (2015) 131.
- [19] M. Wittels, F.A. Sherrill, J. Appl. Phys. 28 (1957) 606.
- [20] C. Miclea, C. Tanasoiu, C.F. Miclea, I. Spanulescu, M. Cioanher, J. Phys. IV Fr. 1289 (2005) 115–120.
- [21] K.E. Holbert, S.S. McCreedy, A.S. Heger, T. Harlow, D.R. Spearing, Performance of piezoresistive and piezoelectric sensors in pulsed reactor experiments, in: Topical Meeting on Nuclear Plant Instrumentation, Controls and Human-Machine Interface Technologies, Columbus, Ohio, 2004.
- [22] B.H. Torby, R.B. Von Dree, J. Appl. Cryst. 46 (2013) 544–549.
- [23] U. Ahmadu, S.S. Ahmad, A.B. Usman, A.M. Muhammad, K.U. Isah, Process. Appl. Ceram. 10 (2016) 79–85.
- [24] A. Onoja, I.M. Umar, I.I. Funtua, L.A. Dim, S.B. Elegba, Nig. J. Phys. 7 (1995) 76–80.
- [25] Ph Ghosez, X. Gonze, J.P. Michenaud, Ferroelectrics 220 (1999) 1–15.
- [26] M. Uludogan, T. Gagın Tur, J. Phys. 30 (2006) 277–285.
- [27] L.S. Cavalcante, V.S. Marques, J.C. Sczancoski, M.T. Escote, M.R. Joya, J.A. Varela, M.R.M.C. Santos, P.S. Pizani, E. Longo, Chem. Eng. J. 143 (2008) 299–307.
- [28] H. Lee, T. Mizoguchi, T. Yamamoto, Y. Ikuhara, Mater. Trans. 50 (2009) 977–983.