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Crystal structure refinement of co-doped $Ba_{0.88}Ca_{0.12}Ti_{0.975}Sn_{0.025}O_3$ ceramic

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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.
- 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.

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ABSTRACT

Ba/Ca-doped barium titanate has been prepared by solid state reaction to produce $Ba_{0.88}Ca_{0.12}Ti_{0.975}Sn_{0.025}O_3$(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/cm^2 (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.

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

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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 $Ba_{0.97}Ca_{0.03}Ti_{0.96}Sn_{0.04}O_3$) [5] and $BaTi_{0.975}Sn_{0.025}O_3$ (c/a = 1.0063, volume = 64.42 Å^3, S.G., *P4mm*-tetragonal) systems [2] with mixed outcomes on phase composition, among others. Results on Rietveld refinement of $BaTi_{1-x}Sn_xO_3$ ($0 \leq x \leq 0.2$) ceramics using neutron powder diffraction showed a crystal which is a mixture of *P4mm* and *Amm*2 (orthorhombic) phases ($0.025 \leq x \leq 0.07$) while other workers [8] on $Ba_{1-x}Sn_xO_3$($0.0 \leq x \leq 0.05$) 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 $Ba_{1-x}Ca_xTiO_3$ ($x = 0.05$ 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) Å^3 and c/a ratio of 1.011 [3]. The solid solution $Ba_{1-x}Ca_xTiO_3$($0.05 \leq x \leq 0.9$) shows the formation of single phase up to $x = 0.3$, whereas it was reported [11] that the thin film system $Ba_{1-x}Ca_xTiO_3$ 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 $Ba_{0.70}Ca_{0.30}TiO_3$ (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 $Ba_{0.88}Ca_{0.12}TiO_3$ (JCPDS81-1288), i.e., same as the Ca concentration in the current work. Sintering at high temperature (1500 °C/6 h) eventually reduced the orthorhombic peaks with consequent reduction in the tetragonal distortion (c/a ~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 $Ba_{1-x}Ca_xTiO_3$ (BCT), provided the molar ratio of (Ba + Ca)/Ti ≥ 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 ~100 °C with fast neutron flux of 1.8×10^{20} n/cm^2 showed the transformation of the tetragonal single crystals to perovskite-type cubic single crystal which are normally stable at 120 °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 $PbZr_{0.5}Ti_{0.5}O_3$ after exposure to a 1 MeV equivalent neutron fluence of 1.7×10^{15} 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 7.6×10^{10} 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