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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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