

**MS13-1-4 In Situ Temperature-Dependent X-ray Diffraction Study of Ferroelectric Single Crystal BCZT
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Abstract

Perovskite ferroelectrics (ABO₃) are enabling components in numerous technological fields, including energy harvesting and storage and electromechanical transducer applications [1]. Among others, lead-free piezoelectric compositions based on Ba_{1-x}(Zr_{0.2}Ti_{0.8})O_{3-x}(Ba_{0.7}Ca_{0.3})TiO₃ (BCZT) have shown promising electromechanical response that can match the currently used Pb(Zr,Ti)O₃-based piezoelectrics [2]. To date, the average crystal structure has only been studied for

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polycrystalline BCZT, revealing rhombohedral (*R3m*), orthorhombic (*Amm2*), tetragonal (*P4mm*), and cubic (*Pm m*) phases in the 80–450 K temperature range [3–6]. Despite this, single crystal structure analysis is important, as it offers information about the crystal symmetry, phase transitions, static configurational displacement, and thermal vibration of each atom without the influence of grain structure. Although several previous studies have succeeded in growing BCZT single crystals [7–11], only Liu *et al.* have reported a high piezoelectric coefficient of 232 pC/N at room temperature for Ba_{0.798}Ca_{0.202}Zr_{0.006}Ti_{0.994}O₃ single crystal that was grown with the spontaneous nucleation method [12]. The relatively high π makes the crystal reported by Liu *et al.* the best candidate for structure investigation.

In this study, and for the first time, *in situ* temperature-dependent single-crystal X-ray diffraction of lead-free ferroelectric perovskite BCZT is reported. The data were collected within the temperature range of 170–380 K, revealing rhombohedral (*R3m*), orthorhombic (*Pmm2*), and tetragonal (*P4mm*) crystal structures. In ferroelectric phases, both B-site and oxygen ions are displaced with respect to the A-site cations at their original position. This shift leads to spontaneous polarization in the crystal, which is the origin of ferroelectricity. Furthermore, the single crystal structure has been modelled via first-principles DFT simulations. The computational investigation aims to get an insight into the local atomic environment of the Zr and Ca dopants and the consequent spontaneous polarization (\mathbf{P}_s). Few previous computational works on BCZT focus on the local atomic environment [13], and the non-stoichiometry makes it challenging to model this single crystal via discrete atom representation and periodic boundary conditions. As a fair compromise, we employed a 3x3x3 supercell featuring 135 atoms, where the fractional proportions are reproduced employing 21, 6, 26, and 1 atoms for Ba, Ca, Ti, and Zr elements, respectively. Starting from pure BaTiO₃, we first introduced the single Zr atom in the Ti sublattice and, consequently, the 6 Ca atoms in the Ba sublattice, isolating and studying the contributions of the two dopants. The structural impact of Zr and Ca atoms is studied by looking at the distance between them and the neighbouring atoms. Whereas the introduction of Zr atom leads to an expected structural expansion, the arrangements of Ca atoms had to be sampled because they play a discriminating role in the relaxation process. Ultimately, the \mathbf{P}_s is evaluated via Berry Phase calculations and Born Effective Charges applied on the atomic displacements derived by computational and experimental structures. The adoption of multiple methods provides us clarity around the gray-zone of the evaluation of this property.

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