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Structural and Ferroelectric Properties of Lead-Free BCT–CFO Magnetoelectric Composites

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Abstract – *This study investigates the structural, piezoelectric, and ferroelectric properties of lead-free Barium Calcium Titanate–Cobalt Ferrite (BCT–CFO) magnetoelectric composites. The samples were synthesized using a solid-state reaction method and characterized using SEM, EDS, and X-ray diffraction techniques. The piezoelectric coefficient (d33) increased significantly after DC poling, reaching 350 pC/N. Ferroelectric measurements revealed a maximum polarization of 3.362 μC/cm², a remnant polarization of 0.762 μC/cm², and a coercive field of 10.274 kV/cm. These results indicate that BCT–CFO composites are promising candidates for energy harvesting and data storage applications.*

Keywords- BCT-CFO, Magnetoelectric composites, Ferroelectricity, Piezoelectricity, SEM

I. INTRODUCTION

Magnetoelectric materials have gained significant attention due to their ability to exhibit both magnetic and ferroelectric properties, enabling strong coupling between electric and magnetic fields. This magnetoelectric effect allows control of magnetic properties using an electric field and vice versa, making these materials highly promising for applications in spintronics and multifunctional devices.

Among these, perovskite-type oxides with the general formula ABO_3 have been widely studied due to their tunable physical properties through cation substitution. Barium Calcium Titanate (BCT) is a lead-free perovskite material known for its high magnetoelectric coefficient, along with excellent dielectric properties, low losses, and good thermal stability. These characteristics make BCT a strong candidate for advanced electronic and energy-related applications.

This work focuses on the structural and ferroelectric properties of BCT-based magnetoelectric composites and explores their potential for practical device applications.

a) Barium Calcium Titanate (BCT)

Barium Calcium Titanate ($BaCaTiO_3$ or BCT) is a lead-free perovskite oxide that exhibits ferroelectric and magnetoelectric properties. It belongs to the $BaTiO_3$ family, where Ca doping modifies the crystal structure and introduces enhanced functional properties. In the perovskite structure, Ba^{2+} ions occupy the corners, Ti^{4+} ions are located at the center, and Ca^{2+} ions influence the lattice through substitution. BCT shows a high magnetoelectric coefficient along with excellent dielectric properties, low loss, and good thermal stability. Due to these characteristics, it is widely used in applications such as sensors, actuators, and energy harvesting devices. Overall, BCT is a promising material for advanced electronic and multifunctional applications.

b) Perovskite Structure

Perovskite refers to a class of materials with the general formula ABX_3, characterized by a well-defined crystal structure. In this structure, the A-site cation (larger ion) occupies the corners of the cubic unit cell, while the B-site cation (smaller ion) is located at the center. The X-site anions (typically oxygen) are positioned at the face centers, forming an octahedral coordination around the B-site cation.

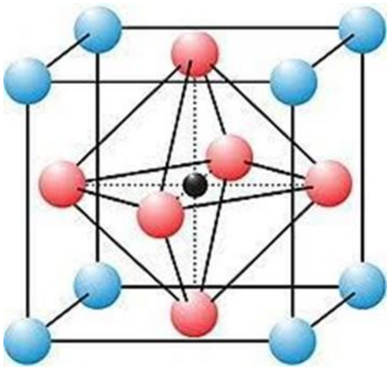


Fig. 1: Schematic representation of perovskite crystal structure (ABX_3).

This unique arrangement allows tuning of physical properties through cation substitution or doping. Perovskite materials exhibit a wide range of properties such as ferroelectricity, piezoelectricity, and high dielectric constant, making them highly suitable for applications in electronic devices, energy systems, and functional materials as shown in Fig. 1, the perovskite structure consists of a cubic lattice with distinct atomic positions.

II. THEORY

a) Ferrites

Ferrites are ceramic magnetic materials composed of iron oxide (Fe_2O_3) combined with other metal oxides such as ZnO, MnO, and NiO. They are electrically insulating but exhibit strong magnetic properties due to ferrimagnetic behavior.

Based on coercivity, ferrites are classified into two types: soft ferrites and hard ferrites. Soft ferrites have low coercivity and are easily magnetized and demagnetized, making them suitable for transformers, inductors, and high-frequency applications. In contrast, hard ferrites possess high coercivity and are used in permanent magnets, electric motors, and storage devices.

Ferrites exhibit ferrimagnetism, where magnetic moments align in opposite directions but do not completely cancel, resulting in net magnetization. Due to their low cost, high stability, and excellent magnetic properties, ferrites are widely used in modern electronic and communication systems.

b) Garnet Ferrites

Garnet ferrites, also known as garnet-type magnetic materials, have the general formula $M_3(Fe_5O_{12})$, where M represents a rare-earth ion such as yttrium. These materials possess a complex crystal structure consisting of three types of lattice sites: tetrahedral, octahedral, and dodecahedral sites. The distribution of iron ions among these sites leads to ferrimagnetic behavior.

Garnet ferrites are characterized by high magnetic permeability, low magnetic losses, and high quality factor (Q-factor). Due to these properties, they are widely used in high-frequency and microwave applications such as isolators, circulators, filters, and magnetic sensors. Their excellent stability and low energy losses make them suitable for advanced communication and radar systems.

c) Spinel Structure

Spinel ferrites have the general formula AB_2O_4, where A is a divalent metal ion (such as Zn^{2+}, Ni^{2+}, or Mn^{2+}) and B is a trivalent ion (typically Fe^{3+}). These materials exhibit a cubic close-packed structure in which oxygen ions form the lattice, and metal cations occupy tetrahedral and octahedral interstitial sites. Based on cation distribution, spinel structures are classified as normal spinel and inverse spinel. In normal spinel, A-site cations occupy tetrahedral positions while B-site cations occupy octahedral sites. In inverse spinel, the cation distribution is rearranged such that half of the B-site cations occupy tetrahedral sites, while the remaining cations occupy octahedral positions.

Spinel ferrites exhibit important magnetic and electrical properties such as high resistivity, moderate magnetization, and low eddy current losses. These characteristics make them suitable for applications in transformers, inductors, electromagnetic devices, and high-frequency electronics.

III. CHARACTERIZATION TECHNIQUES

a. Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is used to study the surface morphology and microstructure of materials. In this technique, a focused beam of high-energy electrons is scanned over the sample surface. The interaction between the incident electrons and the sample produces secondary and backscattered electrons, which are collected to form high-resolution images.

Secondary electrons provide information about surface topography, while backscattered electrons give compositional contrast. SEM analysis is useful for determining grain size, particle distribution, and surface uniformity of the composite.

b. Energy Dispersive X-ray Spectroscopy (EDS)

Energy Dispersive X-ray Spectroscopy (EDS) is an analytical technique used for elemental composition analysis. It is generally coupled with SEM. When the electron beam strikes the sample, it ejects inner shell electrons, and characteristic X-rays are emitted as outer electrons fill the vacancies.

Each element produces X-rays with specific energies, allowing identification of elements present in the sample. EDS provides both qualitative and quantitative information about elemental composition.

c) Piezoelectric Measurement

The piezoelectric effect is the generation of electric charge in a material when mechanical stress is applied. This phenomenon was first observed by Pierre and Jacques Curie in 1880. In addition to the direct effect, the converse piezoelectric effect also exists, where an applied electric field produces mechanical deformation in the material.

Most piezoelectric materials are ferroelectric in nature and exhibit spontaneous polarization that can be reoriented under an external electric field. In polycrystalline ferroelectric materials, the dipoles are randomly oriented, resulting in zero net polarization. Therefore, a poling process is required, in which a strong electric field aligns the domains in a preferred direction. After poling, the material retains remnant polarization, enabling piezoelectric behavior.

The piezoelectric effect is characterized by the piezoelectric coefficient, which represents the relationship between the generated electric charge and the applied mechanical stress, or equivalently, the strain produced under an applied electric field. This coefficient is an important parameter for evaluating the efficiency of electromechanical energy conversion in the material. Piezoelectric materials are anisotropic, meaning their properties depend on the direction of applied stress and polarization. Among various coefficients, the most significant are d_{33} and d_{31}. The coefficient d_{33} represents the polarization generated along the same direction as the applied stress, while d_{31} represents the polarization generated in a direction perpendicular to the applied stress. These coefficients are crucial for assessing the electromechanical performance of piezoelectric materials in practical applications.

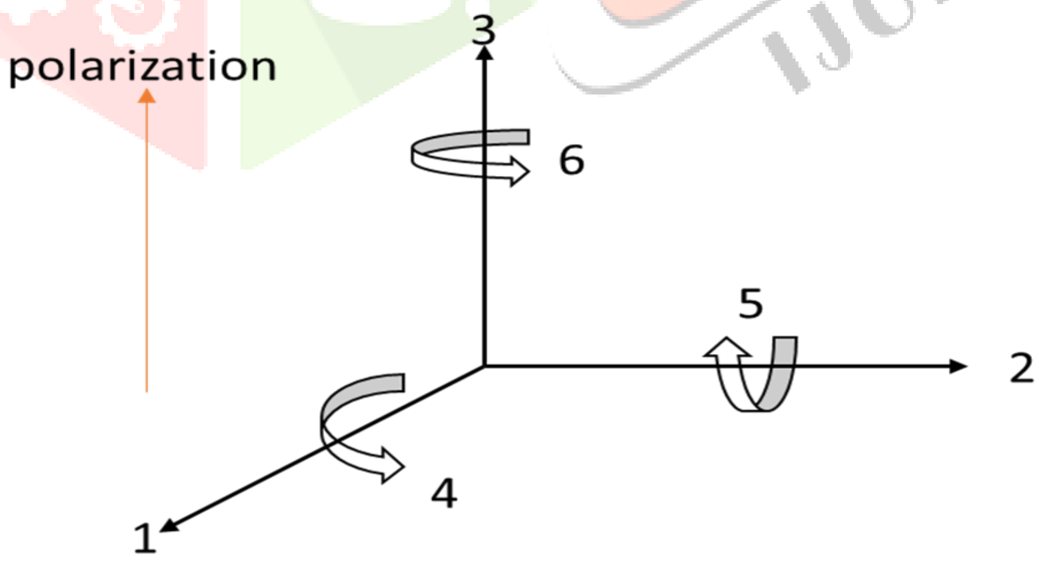


Fig. 2: Direction of force affecting a piezoelectric element

d. Ferroelectric Measurement

Ferroelectric properties are studied using polarization–electric field (P–E) hysteresis loops. When an external electric field is applied, the dipoles within the material align, leading to polarization. As the electric field increases, the polarization reaches a saturation value (Ps). When the electric field is reduced to zero, the material retains a finite polarization known as remnant polarization (Pr). To bring the polarization back to zero, a reverse electric field must be applied, called the coercive field (Ec).

The P–E hysteresis loop provides important information about switching behaviour, energy storage capability, and ferroelectric nature of the material. A well-defined loop confirms strong ferroelectric behaviour.

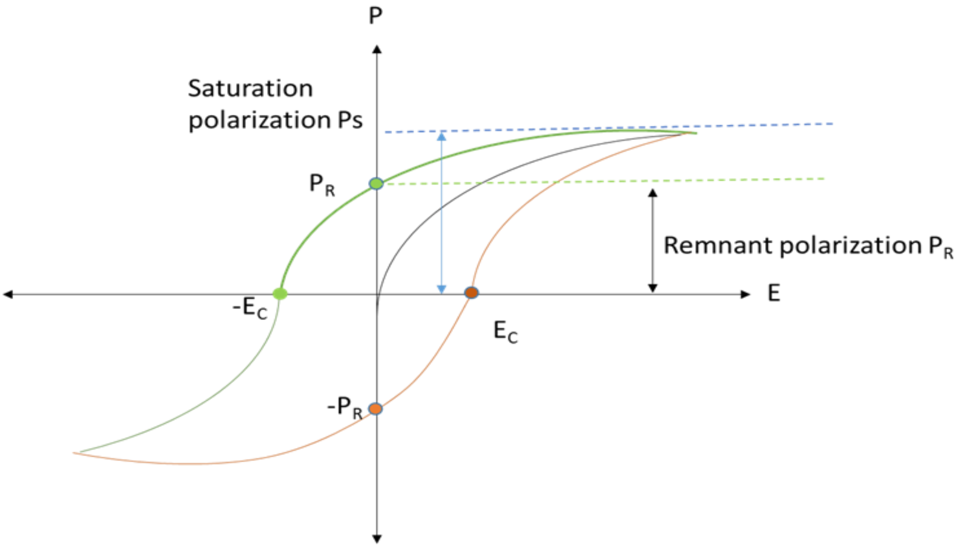


Fig. 3: Typical ferroelectric P–E hysteresis loop.

IV. METHODOLOGY

The BCT–CFO (90%–10%) magnetoelectric composite was prepared using the solid-state reaction method. In this method, the powder of BCT (90%) and cobalt ferrite (10%) were taken in proper proportion. The powders were mixed thoroughly by grinding for about 2 hours to make the mixture homogeneous and to reduce particle size.

Before completion of grinding, a small amount of polyvinyl alcohol (PVA) was added as a binder to improve the strength of the pellets. The mixed powder was then pelletized using a hydraulic press with a die of 1 cm diameter. A total of 7 pellets were prepared.

The prepared pellets were placed in a ceramic boat and heated in a high-temperature furnace. Initially, the pellets were heated at 1000˚C for 5 hours with a heating rate of 2˚C/min. However, proper densification was not achieved, so the pellets were further sintered at 1260˚C for the same duration and heating rate.

After sintering, the pellets were allowed to cool naturally to room temperature. The surfaces of the pellets were then finished using fine polishing paper to obtain smooth surfaces.

Finally, silver paste was applied on both sides of selected pellets to form electrodes. Care was taken to avoid applying silver paste on the edges of the pellets to ensure proper electrical measurements.

Fig. 4: Prepared BCT–CFO pellet after sintering.

V. RESULTS AND DISCUSSION

a. Piezoelectric Properties

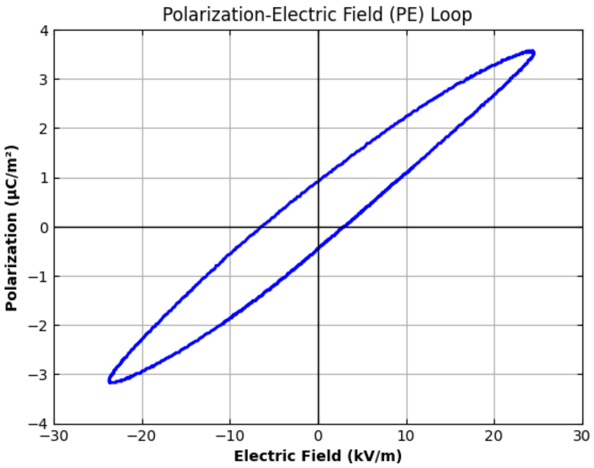
The piezoelectric coefficient (d_{33}) was measured for the given BCT-CFO sample. The value of the piezoelectric coefficient without dc poling is for the give sample is observed the 30 pC/N and the value of the piezoelectric coefficient after dc poling is 350 pC/N by applying the constant force 250 mN. It is a good value of piezoelectric coefficients compared to other references. This means the BCT is more suitable where the direct piezoelectric coefficient is applicable.

Composition	Piezoelectric coefficient (pC/N)
BCT-CFO (90%-10%)	350
BT	180
BZT	44
BCT-BZT	61
BCT	122
BNT-0.3	92
PZT	50

Table1: The piezoelectric value of given sample compared with literature.

b. Ferroelectric measurement:

To predict the usefulness of the given material in the data storage application, ferroelectric measurements were carried out. The P-E measurement shown in the figure conforms to the ferroelectric measurement of the given sample. Ferroelectric measurements take for the given sample for different four higher voltages. Here the thickness of the given sample pellet is 0.9 mm and the area is 45 mm^2. The value of remnant polarisation of the given sample is 3.362 $\mu C/cm^2$, which is essential for storing data for a long time. The squareness ratio of the given sample is 0.2266. The value of coercivity is 10.274 KV/cm, which is used in permanent device applications.



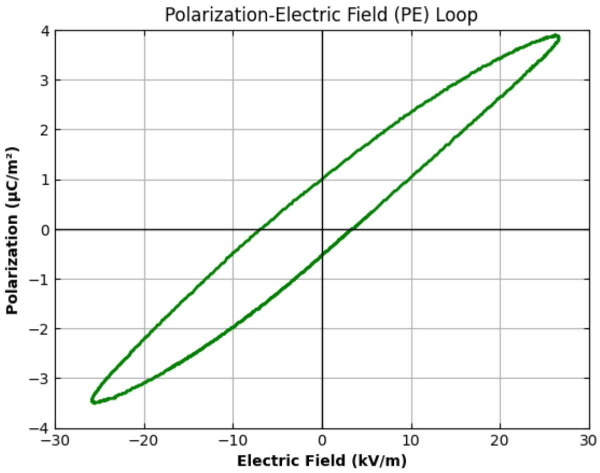


Fig 5: PE loop of BCT-CFO for 12 V(left) and 13 V (right)

composition	P_{max}(μC/cm²)	P_r(μC/cm²)	E_c(KV/cm)	E_{max}(KV/cm)	Squareness ratio
BCT (90%)-CFO (10%)	3.362	0.762	10.274	22.079	0.2266
BCT	16.86	8.44	6.41	90.78	0.500
BZT	13.82	3.24	0.78	45.68	0.234
BT	24.20	10.81	3.02	46.59	0.446
BCT-BZT	12.00	1.19	1.92	63.74	0.099

Table 2: PE loop measurement of sample compared with literature.

c. Morphology and Microstructure:

Surface morphology and topography were studied using SEM as shown in the figure. The particle size of magnetic material is non-uniform. Generally, the particle size of magnetic material is difficult to measure because of two reasons, namely (I) the magnetic particles get agglomerated and (II) the Lorentz force (acted by the magnetic field of the sample) scatters the electrons that lead to the blurred image of the samples. This put the limitation of the SEM imaging. Also, the density of the ME composite is very large.

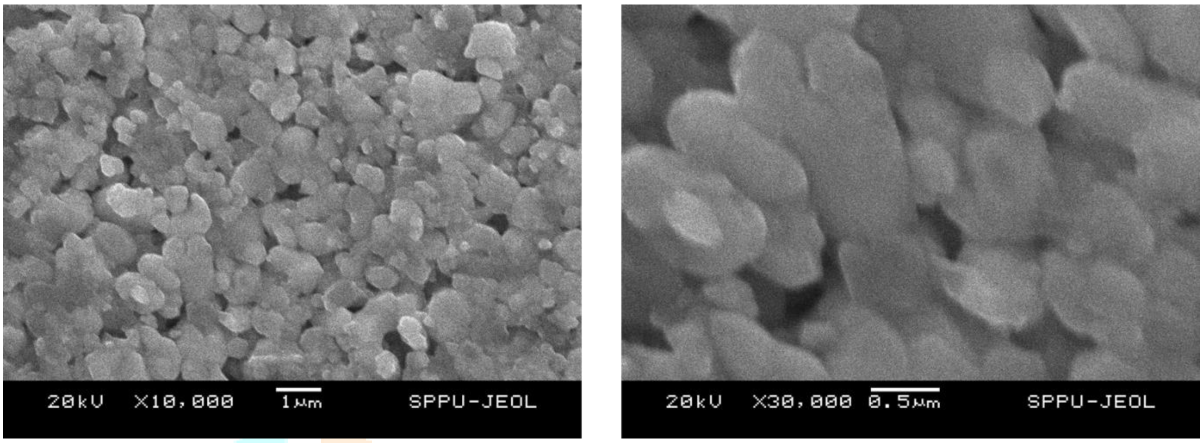


Fig 6: SEM images of BCT-CFO

EDS spectra also confirm the presence of all the elements (Ba, Ca, Ti, Fe, Co, O) without any impurity. The careful observation of the spectra of EDS peaks gives the abundance of elements Ba, Ca, and Ti. The table shows the composition information of the given sample-

Element	**Weight %**	**Atomic %**
O	40.82	76.99
Ca	4.26	3.21
Ba	35.1	7.09
Ti	15.51	9.77
Fe	2.85	1.54
Co	1.55	0.80
Totals	100.00	

Table 3: Elemental composition analysis of sample by using EDS.

VI. CONCLUSIONS

The BCT–CFO composite was successfully synthesized using the solid-state reaction method. The material exhibited a high piezoelectric coefficient (d_{33}) of 350 pC/N after DC poling, indicating strong electromechanical coupling. Ferroelectric measurements confirmed the presence of maximum polarization (3.362 $\mu C/cm^2$), remnant polarization (0.762 $\mu C/cm^2$), and coercive field (10.274 kV/cm), demonstrating good polarization retention and switching behavior suitable for data storage applications. SEM analysis showed non-uniform grain distribution with particle agglomeration, while EDS confirmed the presence of all constituent elements without impurities, indicating successful synthesis of the composite.

Overall, the enhanced piezoelectric and ferroelectric properties make the BCT–CFO composite a promising lead-free material for applications in sensors, actuators, energy harvesting devices, and non-volatile memory systems.

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