Stable piezoelectric response of 0-3 type CaBi$_2$Nb$_2$O$_6$:xwt%BiFeO$_3$ composites for high-temperature piezoelectric applications

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Abstract
Depolarization in the ceramic materials has remained the longstanding obstacle for the materials to be utilized in high-temperature piezoelectric devices. Herein, a strategy to defer thermal depolarization is employed. To acquire the best merits of two different materials, 0-3 type CaBi$_2$Nb$_2$O$_6$:xwt%BiFeO$_3$ (CBN:xwt%BFO) composites are engineered in a unique way by embedding the isolated BiFeO$_3$ (BFO) grains at the grain boundaries of the CaBi$_2$Nb$_2$O$_6$ (CBN) matrix. The composite with 0-3 type connectivity (CaBi$_2$Nb$_2$O$_6$:40wt%BiFeO$_3$) exhibits a high density of 7.98 g/cm$^3$, a high saturated polarization of $\sim$19 μC/cm$^2$, high resistivity of $\sim$10$^{10}$ Ω.cm, and an enhanced piezoelectric coefficient $d_{33}$ of 29 pC/N at room temperature. Composite shows the sharp-peaked ferroelectric–paraelectric transition at high Curie temperature $T_C$ of $\sim$881°C. Importantly, the composite maintains a very high resistivity of $\sim$10$^5$ Ω.cm even at 500°C and the $d_{33}$ of 24 pC/N after annealing at 700°C. Moreover, the poled composite has displayed strong radial and thickness dielectric resonances at 20–700°C. Concluding the results, the CBN:40 wt%BFO composite with 0-3 type connectivity shows the stable high-temperature piezoelectric response much better than either CBN or BFO and is the worthier candidate to be utilized in high-temperature piezoelectric devices.

Keywords
0-3 type composites; CaBi$_2$Nb$_2$O$_6$; BiFeO$_3$; high-temperature piezoelectric
1. Introduction

High-temperature stable piezoelectric materials that can function at high temperatures without failure are desired for structural health monitoring and/or non-destructive evaluation of the next generation turbines, more efficient jet engines, and nuclear/electrical power plants. The operational temperature range of smart transducers is limited for the sensing capability of the piezoelectric material at elevated temperatures [1–3]. Lead-based piezoelectric and ferroelectric oxides such as Pb(Zr0.52Ti0.48)O3 (PZT) and PbMg1/3Nb2/3O3–PbZr0.52Ti0.48O3 has shown large piezoelectric and electromechanical properties at room temperature and are extensively used in sensors and actuators [4–6]. Despite its adaptability to a wide range of distinct applications, PZT contains a large portion of the hazardous lead, raising health and environmental concerns. Moreover, the Curie temperature (Tc) of lead-based materials is commonly below 400°C, which restricts its usage in high-temperature piezoelectric devices [7,8]. Globally in 2019, the estimated market value of piezoelectric devices was $25.1 billion dollars and is expected to boost up more with an annual rate of 6.2% within the coming 5 years [9]. Therefore, tremendous efforts have been put into the development of competitive lead-free high-temperature piezoelectric counterparts.

Bismuth layered structure ferroelectrics (BSFs) are renowned due to their high Tc, low dielectric constant (ε), low aging rate, high resistivity (ρ), and large mechanical quality factor (Qm), which make them potential candidates to be used in high-temperature electronic industry [10,11]. Calcium bismuth niobate, CaBi0.5Nb2O9 (CBN) is a typical BSFs member, which possesses an orthorhombic space group of an A2am phase space and a high Tc of ~940°C, but it suffers from the low piezoelectric coefficient d33 value of 6 pC/N [12]. Wang et al. have reported the d33 value of 16.3 pC/N in modified Ca0.6(Li0.5Bi0.5−xPrx)0.4Bi2O2Nb2O9 ceramic system [13]. Xie et al. has reported the remanent polarization (Pr) of ~10 μC/cm² in the modified Ca0.8Sr0.2Ce0.15Bi0.35Ta0.25Bi2O2Ox ceramics [14]. On the other hand, famous multiferroic, rhombohedral (R3c) BiFeO3 (BFO) maintains its ferroelectric order below its Tc~820°C [15–19]. Novel strain-driven morphotrophic phase boundary (MPB) in highly strained BFO thin films, along with giant ferroelectric polarization of P~100 μC/cm² in (1 1 1) oriented BFO thin films has been reported [20]. Pure BFO ceramic exhibits piezoelectric d33 value higher than ~40 pC/N, but abundant electrons are excited to conduction band due to the low bandgap of ~2.8 eV and the corresponding low resistivity restricts the potential applications of BFO (~400°C) [8,21,22].

In earlier reports, it is clear that the ferroelectric (P, P) and piezoelectric (d33) properties of BFO are better than CBN but the highly resistive behavior and superior temperature range deploying ability of CBN makes it a promising material for high-temperature devices. Thereby, the properties which were hard to achieve at once in a single material, are now possible by combining the multi-phased materials as composites. The combination of CBN and BFO in the form of composite not only requires the competent phases but also the connectivity patterns (0–3, 1–3, 3–3, etc), because symmetry and properties are interconnected [23–25]. Herein following the unique 0–3 type connectivity pattern, highly resistive CBN grains would create the three-dimensional matrix, and isolated high d33 BFO grains would be embedded at the grain boundaries of CBN, in this way merit of both materials can be achieved simultaneously.

Herein, CBN:40 wt%BFO composite with 0–3 type connectivity exhibits larger Pr of 19 μC/cm², enhanced d33 of 29 pC/N much improved than pure CBN ceramic, and Tc of ~881°C. Thermal piezoelectric stability (d33 = 24 pC/N) of the composite is confirmed by annealing the poled sample at 700°C. Strong dielectric anomalies are also observed in fully poled CBN:40 wt%BFO composite at 700°C.

2. Experimental method

A unique approach has been followed for the fabrication of CBN:xwt%BFO (x = 0–80) composite. BFO grains were prepared using high purity Bi2O3 (99.99%, Alfa Aesar, USA), Fe2O3 (99.99%, Alfa Aesar, USA) powders. Powders were weighed with a stoichiometric ratio of BFO, milled for 12 h, dried at 100°C, and pressed under the hydrostatic pressure in the form of pellets adequately. Single-phase BFO ceramics were sintered at 850°C for 10 min by the rapid liquid-phase sinter method [26]. Ceramics were ground to micron-scale level. High purity CaCO3 (99.9%, Aladin, Shanghai, China), Bi2O3 (99.99%, Alfa Aesar, USA), and Nb2O5 (99.9%, Aladin, Shanghai, China) powders were weighed according to the desired stoichiometric ratio of CBN, milled for 24 h, dried overnight at 100°C, and calcined at 850°C for 4 h. Finally, single-phase CBN powder was synthesized by sintering the mixture at 1100°C for 4 h with a rapid heating/cooling rate of 50/100°C/min. Afterward, the CBN and BFO grains were weighed according to the formula of CBN:xwt%BFO (x = 10–80). The composite mixtures were milled, dried, and pelleted into disks of diameter 11 mm and thickness 0.5–0.7 mm under the hydrostatic pressure of 250 MPa. Finally, composites were sintered at 850°C for 1 h with a heating/cooling rate of >50°C/min.

To identify the phase structures of the as-prepared composites, samples were characterized by X-ray Diffraction (XRD), PANalytical, Netherlands, 40 kV, 30 mA, Cu Ka 1λ = 1.54056 Å, step: 0.02°) and then
the simulation of their XRD patterns was carried out to evaluate the lattice parameters of the samples by the Rietveld method. The microstructures and elemental distribution of composites were analyzed by a Field emission scanning electron microscope (FE-SEM, FEI Quanta 200, Hillsboro, OR). Ag electrodes were coated at both surfaces of the disks. Ferroelectric properties ($P-E$ loops) were ascertained at 1 Hz using a ferroelectric analyzer (aixACCT TF Analyzer 2000; Germany) at room temperature. Then, the CBN:xwt%BFO composites were fully polarized in the silicon oil at 80°C, 120°C, and 180°C with a high DC electric field, and the piezoelectric $d_{33}$ coefficient was measured at 60 Hz by using a piezo-$d_{33}$ meter (IAAS ZJ-30, Institute of Acoustics of CAS, Beijing, China). Thermal depolarization was performed after annealing poled samples at specific temperatures (20–900°C) for 1 h; then, $d_{33}$ values were checked when the temperature cooled to room temperature. The DC resistivity as a function of temperature was determined by using an electrometer (Keithley 6517B) for temperatures ranging from 20°C to 500°C with a heating rate of 3°C/min. An LCR analyzer (HP4980A, Agilent) attached to a programmable furnace was used to measure the dielectric permittivity ($\varepsilon_r$) and dielectric loss (tanδ) as a function of the temperature. Dependence of relative dielectric constant ($\varepsilon_r$) and dielectric loss (tanδ) on frequency and dependence of impedance on frequency was measured by Agilent 4294A impedance analyzer. Finally, the electromechanical coupling factors ($k_p, k_t$) and the mechanical quality factor ($Q_{m-kp}$) were calculated through a resonance method.

3. Results and discussion

The co-existence of dual phased orthorhombic CBN and rhombohedral BFO are confirmed in the XRD analysis of CBN:xwt%BFO ($x=30, 40, \text{and } 50$) in Figure 1. Single-phase CBN pattern has been indexed as orthorhombic $A_2\alpha m$ space group [10–14], whereas single-phase BFO is indexed as rhombohedral $R3c$ space group [15–20], which is used for the comparison study of dual phased CBN:xwt%BFO composites. Two sets of peaks are visible after the addition of (xwt%) BFO in the CBN matrix in the middle portion of XRD analysis, the CBN phase remains dominant. Here, (115) is the most intense diffraction plane consistent with the $(112 m + 1)$ of BLSFs [11–13]. An amplified image with diffraction angles 28–35° of single phased CBN and single-phase BFO, along with the dual phased CBN:xwt%BFO ($x=30, 40, \text{and } 50$) is shown in Figure 1(b). In the CBN:xwt%BFO composites ($x=30, 40, \text{and } 50$), the (115)$_D$ and (200/020)$_O$ diffraction peaks are belonging to orthorhombic CBN grains creating a matrix, while split (110)$_D$ diffraction peak is from isolated rhombohedral BFO grains. The intensity of diffraction peak (110)$_D$ of BFO increases as the concentration of BFO increases, but CBN phases remains dominant due to high concentration in the composites. The XRD patterns of other CBN:xwt%BFO

![Figure 1](image-url)  
**Figure 1.** (a) XRD comparison analysis patterns of single-phase CaBi$_2$Nb$_2$O$_9$ ceramic (bottom), pure single-phase BiFeO$_3$ ceramic (top) and dual phased CaBi$_2$Nb$_2$O$_9$xwt%BiFeO$_3$ ($x=30, 40, \text{and } 50$) composites (middle). Inset represents the calculated samples density variation as a function of xwt%BFO in CBN matrix. (b) Amplified $\theta = 28–34^\circ$ XRD analysis of BiFeO$_3$ ceramic, CaBi$_2$Nb$_2$O$_9$ ceramic, and CaBi$_2$Nb$_2$O$_9$xwt%BiFeO$_3$ composites.
compositions \((x = 20, 60, 70, \text{ and } 80)\) are given in the supporting Figure S1(a), where the confirmation about the dual phased behavior of CBN and BFO is visible. The XRD patterns of CBN:xwt%BFO composites were simulated with the Rietveld method and the results unveil the evolution of the crystal lattices and angles dependent on xwt%BFO addition in CBN (Supporting Information Figure S1b, c). The high-symmetric orthorhombic \(A2\text{I}_1am\) structure for CBN and rhombohedral \(R3c\) structure for BFO (a special example of the low-symmetric triclinic \(P1\) structure) are treated individually as reference structures for comparison with experimental XRD data through simulation. The crystal parameters of \(a \parallel b < c\) and \(a = \beta = \gamma = 90^\circ\) prove the typical orthorhombic \(A2\text{I}_1am\) space group for CBN peaks of CBN:xwt%BFO \((x = 0–50)\) composites. Comparing to pure CBN ceramic’s lattice parameters with \(a = b = c = 0.548\) nm and \(c = 2.4897\) nm, small deflection with \(a = b = 0.539\) nm and \(c = 2.45\) nm is observed for CBN:40 wt%BFO composite due to the minor diffusion of Fe from BFO in CBN lattices. Similarly, all CBN:xwt%BFO composites have shown the crystal lattices of \(a = b = c \parallel 0.3942\) nm and the crystal axial angles of \(a = \beta = \gamma \parallel 89.4^\circ\) \(^{[15–17]}\) for BFO indexed peaks, a strong indication of rhombohedral structure. However, it is still a big challenge to exactly simulate the XRD patterns of multiphased (CBN:xwt%BFO) composites. Inset in Figure 1(a) indicates the increasing trend of the experimental density of sintered samples till \(x = 40\) \((\rho = 7.98\) g/cm\(^3\)) as here the 0–3 type connectivity is reported. Isolated BFO grains adjusted well at the grain boundaries of the CBN matrix, overcoming the defects of the samples. Afterward, the value decreases for CBN:50 wt%BFO composite because BFO grains will not remain isolated anymore and 0–3 type connectivity is broken.

The elemental distribution analysis technique has been employed by FE-SEM to confirm the establishment of 0–3 type connectivity of CBN:40 wt%BFO composite. Figure 2(a) shows the surface morphology of pure single-phase BFO ceramics sintered at 850°C for 10 min. There is homogeneity in micron size particles of BFO. Figure 2(b) shows the surface image of single-phase CBN ceramic sintered at 1100°C for 2 h and its density is \(\sim 7\) g/cm\(^3\). Plate-like morphology is observed, which is consistent with the typical characteristic of Aurivillius ceramics due to the anisotropic nature of the crystal structure \(^{[27]}\). Figure 2(c) is the

**Figure 2.** FE-SEM images of (a) BiFeO\(_3\) ceramic, (b) CaBi\(_2\)Nb\(_3\)O\(_9\) ceramic, (c) CaBi\(_2\)Nb\(_3\)O\(_9\) 40 wt%BiFeO\(_3\) composite, (d) Colored elemental mapping by energy–dispersive spectrum recorded from CaBi\(_2\)Nb\(_3\)O\(_9\) 40 wt%BiFeO\(_3\) composite, confirming the 0–3 type connectivity of composite, (e) Elemental distribution of Nb, (f) Elemental distribution of Fe.
cross-sectional SEM image of the CBN:40 wt% BFO composite sample sintered at 850°C for 1 h and its density is \(-7.98 \text{ g/cm}^3\). There exist no holes or cracks in the images, confirming the fabrication of highly dense samples. The fast sintering process suppresses the reaction between the two phases. Here two different size particles are visible, large size particles (2–3 \(\mu\mathrm{m}\)) belong to BFO and the smaller size particles (<1 \(\mu\mathrm{m}\)) belong to CBN grains. The morphological SEM analysis of other CBN\(x\)wt% BFO \((x = 30, 40, \) and \(50\)) compositions are presented in supporting information Figure S2(a, c and e). To analyze the weight percentage of each element in CBN\(x\)wt% BFO \((x = 30, 40, \) and \(50\)) composites, energy dispersive spectrum (EDS) was recorded and presented in supporting information Figure S2(b, d, and f). Theoretical and recorded weight percentages of Fe in the CBN\(x\)wt% BFO composite is compared. The recorded weight percentage of Fe (7.10%) in Figure S2d matches well with our theoretical value (~7.06%). The same behavior of elemental weight percentage is followed for the EDS recorded values and theoretical values. For the confirmation of 0–3 connectivity in CBN:40 wt% BFO, detailed element distribution analysis of CBN and BFO grains is recorded. A typical 2D elemental mapping of CBN:40 wt% BFO is shown in Figure 2(d-f). The Nb elemental distribution (blue color) represents the CBN grains in Figure 2(e), while the Fe elemental distribution (pink color) confirms the presence of BFO grains in Figure 2(f). The CBN (smaller particles) grains have created the 3D matrix in which BFO (large particles) grains are embedded and isolated from each other. It shows that 0–3 type connectivity has been established in CBN:40 wt% BFO composite [23–25,28].

Typical-saturated \(P\)-\(E\) hysteresis loops of CBN\(x\)wt% BFO \((x = 0, 30, 40, \) and \(50\)) composites measured at frequency 1 Hz and at room temperature are shown in Figure 3(a–d). CBN:40 wt% BFO composite has shown the saturated polarization \((P_s)\) of \(-19 \mu\mathrm{C/cm}^2\), which is much better than the single-phase CBN ceramic. All the measurements are taken at the maximum electric field \((E_{\text{max}})\) of 150 kV/cm, this value of \(E_{\text{max}}\) is close to the breakdown electric field of the samples. High electrical resistivity offered by CBN grains allows the implementation of a high poling field, which is important to achieve high-temperature properties [29]. The increase of BFO content in the CBN matrix caused the improvement of ferroelectricity, resulting in an increase in saturated polarization and remnant polarization \((P_r)\). The single-phase CBN ceramic shows the \(P_s\) and \(P_r\) of \(-10.7 \mu\mathrm{C/cm}^2\) and \(-5.8 \mu\mathrm{C/cm}^2\) respectively. CBN:30 wt% BFO, CBN:40 wt% BFO, and CBN:50 wt% BFO show the \(P_r\) values of \(-9.8 \mu\mathrm{C/cm}^2\), \(-11.08 \mu\mathrm{C/cm}^2\) and \(-9.5 \mu\mathrm{C/cm}^2\), respectively. The \(P\)-\(E\) loops of other CBN\(x\)wt% BFO \((x = 20, 60, \) and \(70\)) composites are given in supporting information Figure S3(a–c). Hence, the maximum \(P_r\) value is observed in CBN:40 wt% BFO composition (Supporting information Figure S3d), where 0–3 type connectivity is observed. The ferroelectric

![Figure 3](image-url) Figure 3. The \(P\)-\(E\) hysteresis loops of CaBi\(_2\)Nb\(_2\)O\(_6\):xwt%BiFeO\(_3\) composite with (a) \(x = 0\), (b) \(x = 30\), (c) \(x = 40\), (d) \(x = 50\).
polarization (i.e. surface polarization charge per unit area) is calculated by measuring the current when an electric field is employed. Therefore, enhancement in the values of $P_s$ and $P_r$ are mainly associated with BFO grains possessing higher surface polarization charges than CBN particles under a same electric field. The decrement in the value of $P_r$ at $x = 50$ is due to the high BFO content which has passed the percolation threshold, so afterward high leakage screens some polarization during measurement [23, 24, 30].

Leakage current has a vital influence on the ferroelectric and piezoelectric performance of the materials. Figure 4(a) is representing the dependence of leakage current on the electric field ($E$) for CBN:xwt%BFO ($x = 0$, 30, 40, and 50) composites, measured at room temperature. Low leakage current value of $\sim 4.9 \times 10^{-7}$ A has been observed for pure CBN ceramic at 100 kV/cm. Electrical insulation has decreased gradually with the increment of BFO content from 30 to 50 wt%. Large leakage current value of $\sim 2.4 \times 10^{-6}$ A at 100 kV/cm is detected for CBN:50 wt%BFO composite. As already discussed in the explanation of $P$-$E$ loops, at $x = 50$ the percolation threshold has passed and the influence of high content BFO has introduced the high leakage current. BLSP’s are renowned because of their highly resistive behavior. CBN:xwt%BFO ($x = 0$–50) composites have shown the high resistivity of $\sim 10^{10}$ $\Omega$.cm at room temperature and $\sim 10^5$ $\Omega$.cm at a high temperature of 500°C. In Figure 4(b), the temperature-dependent resistivity ($\rho$-$T$) plots of pure BFO and pure
CBN ceramics, along with the CBN:xwt%BFO (x = 30, 40, and 50) composites are shown. Consistent behavior with previous reports, pure BFO ceramic has shown a high resistivity of $\sim 10^9 \, \Omega \cdot cm$ at room temperature but rapidly reduced to $\sim 10^3 \, \Omega \cdot cm$ at 300°C. As compared to BFO ceramic, the resistivity of pure CBN ceramic and CBN:xwt%BFO (x = 30, 40, and 50) composites have decreased steadily and no sudden drop has been observed in the temperature range of 20–500°C. Most importantly, pure CBN ceramic and CBN:40 wt%BFO composite with 0–3 type connectivity has shown a high resistivity of $\sim 10^{10} \, \Omega \cdot cm$ at room temperature, which gradually drops to $\sim 10^5 \, \Omega \cdot cm$ at 500°C. This similar behavior in samples is because highly insulating CBN grains have created the three-dimensional matrix around BFO grains. In this way BFO grains remain isolated from each other, resulting in that the leakage current of BFO grains can not influence at high temperatures in the composite sample. CBN:50 wt%BFO composite is showing more conductive behavior among all composite samples, with the lowest resistivity of $\sim 0.25 \times 10^4 \, \Omega \cdot cm$ at 500°C. The main reason is the breakdown of 0–3 type connectivity among BFO and CBN grains at 50 wt%BFO. The high content of BFO grains has introduced the high leakage current and low resistive behavior in the composite.

Figure 5(a) represents the dependence of piezoelectric coefficient $d_{33}$ of CBN:xwt%BFO (x = 0, 20, 30, 40, and 50) composites poled at 80°C, 120°C and 180°C. A high poling field of 150 kV/cm is employed to achieve a high piezoelectric property. Unlike perovskite piezoelectric ceramics which possess a low coercive field to polarize completely, CBN-based materials are difficult to polarize completely at a low coercive field and thus requires a high poling field [31]. It is evident that when samples were poled at 180°C, maximum values of $d_{33}$ were achieved for all samples. All the CBN:xwt%BFO (x = 20, 30, 40, and 50) composite samples have higher $d_{33}$ values than the $d_{33}$ value of pure CBN ceramic (9 pC/N). Increasing ($d_{33}$ versus xwt %BFO) trend is visible for all temperature values, CBN:40 wt%BFO composite with 0–3 type connectivity poled at 180°C has given the maximum $d_{33}$ value of $29 \, pC/N$ at room temperature. In CBN:40 wt%BFO composite, BFO grains (with grain size 2–3 μm) present at the surface introduce high charge and contribute a large $d_{33}$ (pC/N) value than CBN grains (with grain size <1 μm) during piezoelectric effect measurements under the external stress. Meanwhile, during inverse piezoelectric measurements, most of the BFO grains inside the composite introduce high strains and contribute a large $d_{33}$ (pm/V) value than CBN grains under the external AC electric field. Afterward, the $d_{33}$ value for CBN:50 wt%BFO has reduced to 25 pC/N which is consistent with the reduction of domain switching (percolation threshold) in the P–E loops. In particular, the $T_g$ region of BiFeO$_3$-based ceramics (~400°C) has been ignored for several years, although it is an effective medium to engineer/enhance properties via 0–3 type connectivity. Stable piezoelectric response at high temperatures suggests that CBN:50 wt%BFO sample has achieved this effect.

![Figure 5](image_url)

**Figure 5.** (a) Piezoelectric coefficient ($d_{33}$) as a function of x value in CBN:xwt%BFO composites at different poling temperatures (80°C, 120°C, and 180°C) (b) Piezoelectric coefficient $d_{33}$ of the poled CBN:xwt%BFO composites, annealed at 28–900°C. (c) The impedance as a function of frequency behavior of CBN:xwt%BFO (x = 0, 30, 40, and 50) composites at room temperature. (d) Electromechanical coupling factors ($k_p$ and $k_t$), and quality factor ($Q_{m,K}$) of the CBN:xwt%BFO composites.
temperature is a critical requirement of any piezoelectric ceramics used in wide temperature range piezoelectric devices [1–3]. Thermal-depoling behavior of CBN:xwt% BFO (x = 0, 20, 30, 40 and 50) composites are displayed in Figure 5(b), where piezoelectric coefficient $d_{33}$ (pC/N) is plotted against annealing temperature range 20–900°C to observe the degradation temperature ($T_d$) of the composites. CBN:xwt% BFO (x = 20, 30, 40, and 50) composites have shown a similar degradation trend, $d_{33}$ values almost remained same till 700°C, and then dropped swiftly between 700°C and 900°C, confirming that 700°C is the degradation temperature of the composites. After annealing the pooled samples at 700°C, the room temperature measured $d_{33}$ values of pure CBN ceramic, CBN:20 wt% BFO, CBN:30 wt% BFO, CBN:40 wt% BFO, and CBN:50 wt% BFO are 9 pC/N, 14 pC/N, 17 pC/N, 24pC/N, and 22 pC/N, respectively. Afterward, annealing at 900°C, the $d_{33}$ value of pure CBN remains 3 pC/N but for all composites, it turns to zero. The $d_{33}$ drops rapidly when the annealing temperature is near to that of Curie temperature ($T_C$), and almost turns to zero after the annealing temperature is above $T_C$. At high temperature, stable and high $d_{33}$ value suggests that CBN:40 wt% BFO composite is a high-quality high-temperature piezoelectric material, suitable for utilization in high precision actuator applications with excellent temperature stability [32,33]. Impedance-frequency plot of poled CBN:xwt% BFO (x = 0, 30, 40, and 50) composites with similar thickness and diameter are displayed in Figure 5(c), showing the radial and thickness anomalies at ~160 kHz and ~2.03 MHz.

After that, the planar electromechanical coupling factor ($k_p$), thickness electromechanical coupling factor ($k_t$), and mechanical quality factor ($Q_{m-qp}$) are calculated under piezoelectric IEEE standard [34]. Composite CBN:40 wt% BFO with 0–3 type connectivity has shown the $k_p$ of 0.301, $k_t$ of 0.53, and the $Q_{m-qp}$ of 446 at room temperature, which is best among CBN: xwt%BFO (x = 0–50) composites (Figure 5(d)). The $k_p$ and $k_t$ values of CBN:xwt% BFO (x = 20, 30, 40, and 50) composites are much better than pure CBN ceramic. The unique 0–3 type connectivity pattern in which the highly resistive CBN grains have created the three-dimensional matrix, while isolated high $d_{33}$ BFO grains are embedded at the grain boundaries of CBN. The nonconducting CBN particles are acting as barriers between the BFO particles. In a word, these three-dimensional barriers increase the coupling factor of the composite. Furthermore, for the explanation of the calculation of $k_p$ and $k_t$ the required equations and parameters are described in the Supplementary Information Table S1.

Figure 6(a-d) shows the temperature dependence of the dielectric permittivity ($\varepsilon_r$) of CBN:xwt% BFO (x = 0, 30, 40, and 50) composites, suggesting the high $T_C$ >850°C. As earlier reported Curie temperatures of pure CBN ceramic and pure BFO ceramic are 940°C and 820°C, respectively, [15–22]. Hence, the $T_C$ of CBN:xwt% BFO (x = 30, 40, and 50) composites must be within this range 820–940°C. The values of dielectric constant increase with the increase of temperature, because temperature affects the orientation of polarization [27]. Figure 6(a-d) shows the dielectric versus

![Figure 6](image-url)
temperature trend for pure CBN and CBN:xwt%BFO (x = 30, 40, and 50) composites at different frequencies of 10 kHz, 100 kHz, and 1 MHz, respectively, within the temperature range of 0–1000°C. Sharp peaked dielectric permittivity at 948°C is due to the ferroelectric to the paraelectric phase transition of the pure single phased CBN ceramic in Figure 6(a). This behavior is consistent with earlier reported results [35]. The values of $T_C$ shift slowly but surely from 948°C to 855°C for CBN:xwt%BFO (x = 0, 30, 40, and 50) composites, signifying the strong influence of varying BFO content in CBN:xwt%BFO composites. Herein, the $T_C$ values of CBN:30 wt% BFO, CBN:40 wt% BFO, and CBN:50 wt% BFO are 915°C, 881°C, and 855°C, respectively. The $T_C$ values of CBN:xwt%BFO (x = 30, 40, and 50) composites are well confirmation of the thermal-depoling values of $d_{33}$ at 850°C (Figure S5(b)). The $\varepsilon_r$ value of CBN:40 wt% BFO with 0–3 type connectivity is 2010.11 at 881°C for 10 kHz frequency (Figure 6(c)), which is much higher than that of pure CBN ceramic ($\varepsilon_r$ = 930.4) and other composites. A relatively small dielectric loss (tan $\delta$) value is observed for all the CBN:xwt%BFO (x = 0, 30, 40, and 50) composites (Supporting Information Figure S3a-d).

In Figure 7(a-d) the dielectric properties and piezoelectric response of fully polarized pure CBN ceramic and CBN:40 wt% BFO composite are studied by their dielectric resonances within the temperature range of 100–700°C. Due to the piezoelectric $d_{33}$ and $d_{31}$ effects, the poled composites deform and vibrate along with thickness and radial directions, respectively, at a 0.5 V AC voltage, which introduces impedance (Figure 5(c)) and dielectric anomalies [36,37]. At 100°C for 1 kHz, the $\varepsilon_r$ value of pure CBN ceramic is ~433 (Figure 7(a)) which has increased to ~545 for CBN:40 wt% BFO (Figure 7(c)). Such increase of $\varepsilon_r$ in CBN:40 wt%BFO composites is largely attributable to the micro-capacitor effect of interphases at the grain boundaries of CBN and BFO grains. Samples depolarize and turn out to be conductive with rising temperature and in consequence, their dielectric anomalies become fragile and finally vanish in close proximity to their $T_C$ [38]. At 700°C, the calculated $k_p$ value of poled CBN:40 wt% BFO composite is 0.265, compared with 0.301 at 20°C (14% less). Even though the amplitudes of resonance (at 229.28 kHz) and antiresonance frequencies (at 222.3 kHz) have reduced with the increment in temperature; however, it still confirms an approximately identical value of $k_p$. Therefore, dielectric anomalies in CBN:40 wt% BFO remain temperature-independent up to 700°C (inset Figure 7(c)) due to the high $T_C$ values of pure BFO (823°C and pure CBN (948°C). Moreover, the dielectric loss (tan $\delta$) of pure CBN ceramic measured at 100 kHz steadily increases from ~0.8% to 1.4% (Figure 7(b)) and for CBN:40 wt%BFO composite increases from 1.3% to 2.9% (Figure 7(d)) by increasing the temperature from 100°C to 700°C. High resistance at 500°C, stable piezoelectric $d_{33}$ response at 700°C and low dielectric loss also at 700°C suggests the high composite density, less holes/cracks, and the existence of fewer charged defects (such as oxygen vacancies) after sintering the composites at 850°C. This work presents considerable information regarding

![Figure 7](image-url)  
Figure 7. Dependence of relative dielectric constant ($\varepsilon_r$) and dielectric loss (tan $\delta$) on frequencies at 100–700°C for (a, b) Pure CBN ceramic and (c, d) CBN:40 wt% BFO composite, where amplified insets images verify the dielectric anomalies at 700°C.
4. Conclusions

Well-engineered 0–3 type CBNxwt%BFO composite has been fabricated to simultaneously utilize the best merits of CBN with high-temperature resistivity and BFO with larger piezoelectric coefficient in a single material. The micro-image analysis of CBN:40 wt%BFO composite authenticates the isolation of BFO grains from each other and their embedment at the grain boundaries of the CBN matrix. CBN:40 wt%BFO composite with 0–3 type connectivity shows a high density of 7.98 g/cm³, enhanced $P_c$ of 11.08 μC/cm², high resistivity of $\sim 10^{10}$ Ω·cm, high $d_{33}$ of 29 pC/N, a $k_p$ of 0.301, a $k_t$ of 0.53, and a $Q_{m-kp}$ of 446 at room temperature. A high Curie temperature of $\sim 881\,^\circ$C is measured for the composite, indicating toward the high thermal-depoling behavior. As a comparison at high temperatures, the resistivity of CBN:40 wt%BFO composite is $\sim 10^5$ Ω·cm at 500°C. A strong piezoelectric response is confirmed at 20–700°C by the measurement of $d_{33}$ (24 pC/N at 700°C) and dielectric resonance/anti-resonance anomalies in the fully polarized CBN:40 wt%BFO composite. The $k_p$ remains almost stable by increasing the temperature to 700°C, signifying its prospective utilization toward high-temperature piezoelectric devices.

Disclosure statement

No, potential conflict of interest was reported by the authors.

Funding

The work is supported by the Higher Education Commission of Pakistan start-up research [grants No: 21-2344/SRGP/R&D/HEC/2019 and 21-2340/GRG/R&D/HEC/2019].

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Supporting Information

Supporting information is available.

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