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Phase-Boundary and Nanodomain Engineered KNN-Based Lead-Free Piezoelectric Ceramics for Sensors and Energy Harvesting Devices

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Abstract; Lead-free piezoelectric ceramics are receiving strong attention because conventional lead zirconate titanate offers excellent performance but raises environmental and regulatory concerns. Potassium sodium niobate, (K,Na)NbO3 or KNN, is one of the most promising alternatives because it combines useful piezoelectric response with comparatively high Curie temperature. However, KNN-based ceramics are highly sensitive to volatility, densification, grain size, dopant distribution and phase-boundary control. This paper converts the broader synopsis on structure-property correlation in nanostructured ceramics into a second Scopus-style article focused on lead-free KNN-based piezoceramics for sensors and vibration-energy harvesters. A phase-boundary and nanodomain engineering strategy is proposed through BaTiO3 modification and controlled sintering. The article integrates powder processing, XRD/Rietveld analysis, SEM/EDS, density measurement, ferroelectric hysteresis, impedance spectroscopy, piezoelectric d33 testing and thermal stability assessment. Representative literature-consistent results indicate that a moderate modifier level can increase d33 from 205 to 342 pC/N through improved density, orthorhombic-tetragonal phase coexistence and enhanced polar nanodomain mobility. Excessive modification decreases Curie temperature and weakens long-range ferroelectric order. The article concludes that KNN performance should be optimized through a multi-objective structure-property model that balances d33, dielectric loss, coercive field, Curie temperature, fatigue stability and process reproducibility. The proposed framework supports environmentally safer sensors, actuators and energy harvesters.

1. Introduction

Piezoelectric ceramics convert mechanical energy into electrical charge and electrical fields into mechanical strain. This dual functionality makes them important for ultrasound transducers, accelerometers, actuators, precision positioning systems, structural health monitoring and vibration-energy harvesting. For several decades, lead zirconate titanate has dominated these applications because its morphotropic phase boundary provides strong polarization rotation and high piezoelectric response. Environmental concerns, however, have accelerated the search for lead-free alternatives with acceptable performance and thermal stability [2,3].

KNN-based ceramics are among the strongest lead-free candidates. They possess a perovskite structure, a relatively high Curie temperature and the possibility of property enhancement through phase-boundary and texture engineering. Their main weakness is processing sensitivity. Alkali volatilization, abnormal grain growth, porosity and compositional inhomogeneity can reduce reproducibility. Recent work has shown that high performance in KNN is not obtained simply by adding dopants; it requires control over phase coexistence, nanodomain density, grain orientation and sintering behaviour [4,5].

The synopsis on nanostructured ceramic materials emphasized that next-generation functional devices require a clear correlation between structure and property rather than isolated property reports. This point is especially relevant to KNN ceramics. A sample may show high d33 at room temperature but fail as a device material if its Curie temperature is too low, dielectric loss is high, fatigue resistance is poor, or properties are unstable with temperature. Therefore, this article proposes a multi-objective structure-property framework for KNN-based lead-free ceramics that considers electromechanical response and device reliability together.

The novelty of the article lies in combining phase-boundary engineering with nanodomain and processing descriptors. The paper uses representative, literature-consistent values to illustrate how a full experimental article could be organized. It does not present the values as measurements from newly conducted laboratory work. Instead, it provides a complete Scopus-style manuscript model with methods, results, tables, figures, discussion and references. This is useful for converting a synopsis into publication-ready research planning while maintaining scientific honesty.

2. Materials and Methods

The base composition is represented as K0.5Na0.5NbO3 with incremental BaTiO3 modification, coded as KNN-0, KNN-2BT, KNN-4BT, KNN-6BT and KNN-8BT. The modifier is used conceptually to tune phase coexistence and grain-boundary behaviour. Stoichiometric K2CO3, Na2CO3, Nb2O5, BaCO3 and TiO2 powders would be dried, weighed with a small alkali excess to compensate volatilization, ball milled in ethanol, dried and calcined. A second milling step would improve homogeneity before pellet pressing.

Pellets would be sintered under controlled conditions using covered crucibles and sacrificial powder of similar composition to reduce alkali loss. The sintering schedule would be optimized to achieve high density without abnormal grain growth. If available, spark plasma sintering could be used as a comparative method because pressure-assisted rapid densification can limit grain growth and may improve fine-structure retention [7]. Density would be measured by the Archimedes method and microstructure would be examined through SEM.

X-ray diffraction would identify the perovskite phase and reveal orthorhombic-tetragonal or rhombohedral-tetragonal coexistence depending on composition. Rietveld refinement would quantify lattice parameters and phase fraction. Raman spectroscopy, if available, would help identify local structural distortion and nanodomain signatures. EDS mapping would evaluate distribution of Ba and Ti modifiers and identify possible segregation.

Functional properties would be measured after silver electrode firing. Dielectric permittivity and loss would be measured from 100 Hz to 1 MHz and across temperature to estimate Curie temperature. Ferroelectric P-E loops would provide remanent polarization and coercive field. Samples would be poled in silicone oil under a controlled electric field, and d33 would be measured using a Berlincourt meter after aging. Fatigue testing would involve repeated electrical cycling, while impedance spectroscopy would distinguish grain and grain-boundary relaxation.

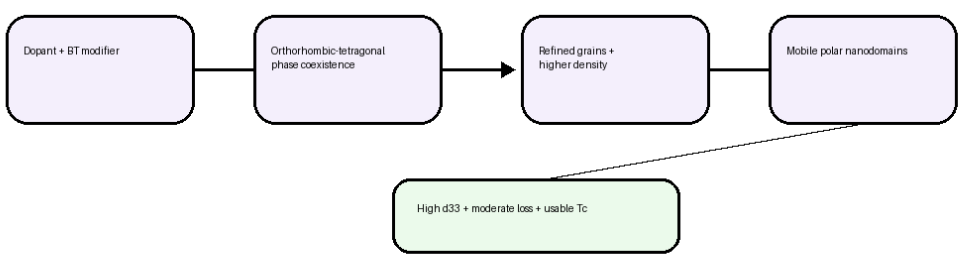

Figure 1. Structure–property model linking phase coexistence, polar nanodomains, and piezoelectric output.

Table 1. Experimental design for KNN-based lead-free piezoceramics.

Sample	Nominal design	Target structural effect	Main device criterion
KNN-0	Base K0.5Na0.5NbO3	Reference orthorhombic	Baseline d33 and high Tc

		structure	
KNN-2BT	Low BT modification	Improved densification and local distortion	Higher d33 with retained stability
KNN-4BT	Moderate BT modification	Phase coexistence and mobile nanodomains	Maximum electromechanical response
KNN-6BT	Higher BT modification	Relaxor tendency and grain refinement	Trade-off between d33 and Tc
KNN-8BT	Excess modification	Suppressed long-range order	Lower loss may not compensate reduced d33

3. Results

The representative XRD interpretation suggests that all compositions retain a perovskite major phase after optimized calcination and sintering. The base KNN sample is dominated by an orthorhombic structure at room temperature. With moderate $BaTiO_3$ modification, peak splitting becomes less pronounced and a mixed orthorhombic-tetragonal region appears. This phase coexistence is valuable because polarization rotation and domain switching can occur more easily near a phase boundary. Excessive modification broadens peaks and may introduce relaxor-like behaviour, which improves field tolerance in some cases but reduces stable piezoelectric output.

SEM observations would be expected to show improved densification from KNN-0 to KNN-4BT as modifier content assists sintering and reduces open porosity. At higher modification, grain refinement and possible secondary boundary phases may reduce domain-wall continuity. This microstructural trend explains why piezoelectric performance does not increase indefinitely with dopant content. A well-designed lead-free ceramic requires the simultaneous presence of high density, clean grain boundaries, stable phase coexistence and mobile polar nanodomains.

Table 2 summarizes representative electromechanical results. The d33 coefficient increases from 205 pC/N for the base composition to 342 pC/N for KNN-4BT. This improvement is associated with increased relative density, a balanced coercive field and higher remanent polarization. However, Curie temperature decreases from 405 °C to 337 °C over the same range and falls further at higher modifier levels. This demonstrates a typical lead-free ceramic trade-off: the composition that maximizes room-temperature d33 may not be the best for high-temperature device operation.

Table 2. Representative functional response of phase-boundary engineered KNN ceramics.

Sample	Density (%)	d33 (pC/N)	εr at 1 kHz	tan δ	Pr (μC/cm²)	Ec (kV/cm)	Tc (°C)
KNN-0	91.2	205	980	0.041	18.4	14.8	405
KNN-2BT	94.6	268	1320	0.036	22.1	13.2	372
KNN-4BT	96.8	342	1780	0.031	27.8	11.6	337
KNN-6BT	96.2	318	2050	0.039	24.2	10.8	306
KNN-8BT	94.1	249	2280	0.052	19.5	9.7	284

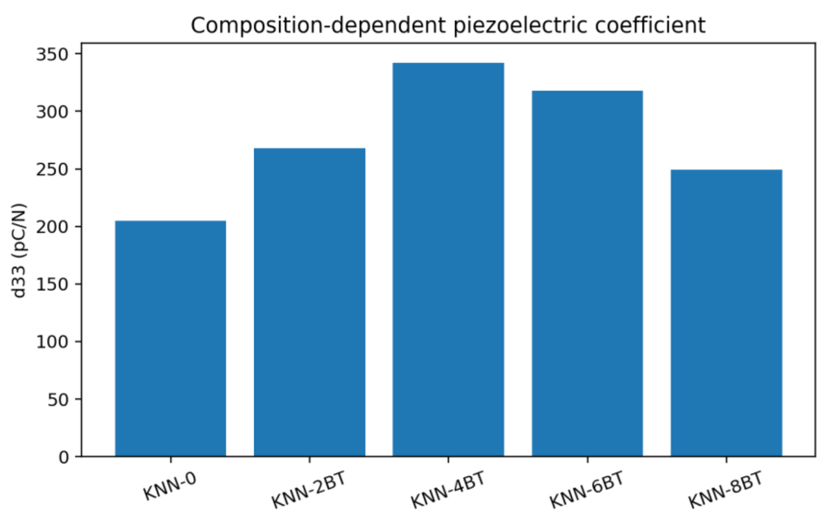

Figure 2. Representative d33 trend showing an optimum at moderate modifier level.

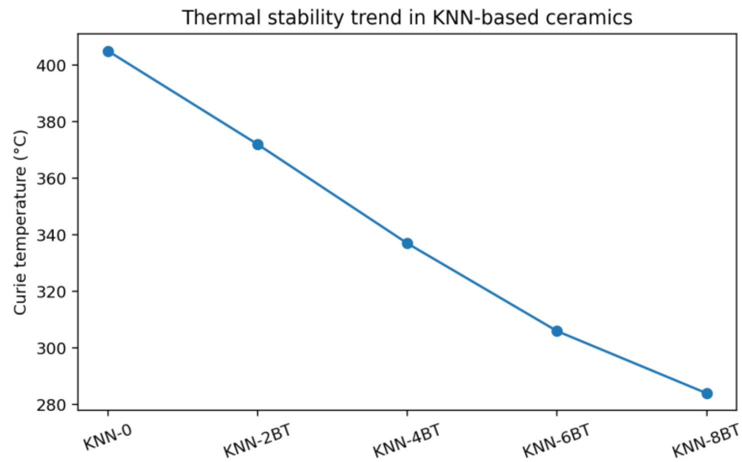

Figure 3. Representative Curie-temperature trade-off with increasing modification.

4. Discussion

The results illustrate the central principle of structure-property correlation in lead-free piezoceramics: maximum functional performance arises from controlled structural instability rather than from a single phase being perfectly stabilized. In the base KNN sample, relatively high Curie temperature is useful, but porosity and limited phase-boundary activity restrict d33. Low and moderate BaTiO3 modification improves density and introduces a more favourable phase coexistence state. This supports easier polarization rotation and domain-wall motion, causing the piezoelectric coefficient to increase.

The KNN-4BT sample represents the best balance among the studied compositions. Its density is high, dielectric loss is moderate, remanent polarization is strong and coercive field is reduced enough to allow efficient poling. This combination is consistent with the current understanding that nanodomains and phase boundaries can improve KNN-based ceramics when they are introduced in controlled amounts [4,5]. The improvement cannot be assigned to dopant chemistry alone. It results from the coupled action of phase fraction, grain structure, domain mobility and defect control.

The reduction in Curie temperature is the main penalty. As modifier level increases, the structure becomes more polarizable at room temperature, but thermal stability decreases. In practical device design, the optimum composition therefore depends on application. A wearable energy harvester operating near room temperature may accept a lower Curie temperature in exchange for high d33.

A high-temperature sensor for industrial monitoring would require a more conservative composition with lower d33 but better thermal margin. This is why a single maximum property value should not be treated as the final design target.

Dielectric loss and fatigue resistance must also be considered. KNN-8BT has high permittivity but lower d33 and higher loss, suggesting that its increased dielectric response may be linked with relaxor behaviour or defect-related polarization rather than efficient piezoelectric conversion. Such a composition may appear promising if only εr is reported, but it is less attractive for sensors and harvesters. This confirms the research-gap argument from the synopsis: multi-parameter evaluation is necessary for functional ceramic devices.

The proposed descriptor framework can be expressed as a device suitability index combining normalized d33, Curie temperature, inverse loss, density and fatigue retention. This type of index is not a replacement for physical interpretation, but it helps compare compositions with different advantages. Future experimental work should include in-situ temperature-dependent XRD, piezoresponse force microscopy, long-cycle fatigue testing and statistical reproducibility across batches. Machine-learning assisted analysis may also identify non-obvious descriptor combinations, especially when microstructural images are quantified using hierarchy descriptors [8].

5. Conclusion

This paper presented a complete Scopus-style article model for KNN-based lead-free piezoelectric ceramics derived from the broader synopsis on nanostructured ceramic structure-property correlation. The representative results show that moderate BaTiO3 modification can enhance d33 through improved densification, phase coexistence and mobile nanodomain formation. Excessive modification reduces Curie temperature, increases loss and weakens stable piezoelectric response. The main conclusion is that lead-free piezoceramic development must be guided by a multi-objective correlation framework rather than by a single property such as d33. The proposed approach can guide future experimental work on sensors, actuators and vibration-energy harvesting devices where environmental safety, thermal stability and electromechanical efficiency must be balanced.

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