

Lead-Free KNN Piezoelectric Stack Actuators for Semi-Active Suspension Control: Correlating Fabrication, Microstructure, and Electromechanical Performance

Yan Duan*

Faculty of Vehicle Engineering, Chongqing Industry Polytechnic University, Chongqing, 401120, China
received December 4, 2025; received in revised form January 6, 2026; accepted January 16, 2026

Abstract

This study reports on the design, processing, and functional assessment of Li/Sb/Ta-modified $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ ceramics targeted for environmentally compliant high-force actuators in automotive vibration management. Ten compositions were synthesized on the basis of solid-state reaction with sintering between 1 050 and 1 150 °C, and multi-scale characterization combined *in situ* high-temperature XRD, SEM, HRTEM, Raman spectroscopy, XPS, EBSD, BET analysis, dielectric spectroscopy, and impedance measurements with actuator-level electromechanical testing. Compositional tuning established an orthorhombic-tetragonal coexistence window in which the benchmark composition $(\text{K}_{0.45}\text{Li}_{0.05})(\text{Na}_{0.47}\text{Li}_{0.03})(\text{Nb}_{0.90}\text{Sb}_{0.06}\text{Ta}_{0.04})\text{O}_3$ exhibits 58 % orthorhombic and 42 % tetragonal phases, an O-T transition at 195 °C, and a Curie point above 380 °C. At an optimized sintering temperature of 1 100 °C this ceramic reaches a density of 4.59 g/cm³ (99.2 % theoretical), grain sizes of about 2.4 μm, and a specific surface area of 1.2 m²/g, together with $\epsilon_r = 1\,850$ and $\tan\delta \approx 2.5\%$ at 1 kHz. Moderate oxygen vacancy contents around 7.5 % balance grain-boundary softening and insulation, yielding $d_{33} = 432\text{ pC/N}$, $k_p = 0.45$, $\text{Pr} = 28.7\text{ μC/cm}^2$, and $E_c = 12.4\text{ kV/cm}$. Long-term reliability is demonstrated by 94.3 % retention of d_{33} after 1 000 h aging at 85 °C and only 6.8 % degradation after 10⁶ bipolar cycles at 50 Hz. Prototype 10-layer multilayer devices fabricated from the optimized composition show stable displacement response under fields of several kV/mm, confirming the potential of these lead-free ceramics for robust, RoHS-compliant smart suspension hardware. The integrated processing-structure-property correlations established here provide a transferable framework for tuning phase boundaries and defect chemistry in next-generation lead-free actuator ceramics for automotive applications.

Keywords: Phase boundary engineering, relaxor ferroelectricity, defect-mediated conduction, multilayer ceramic devices, automotive vibration isolation

1. Introduction

The global transition toward environmentally sustainable materials in functional ceramics has intensified research into lead-free piezoelectrics as viable replacements for traditional $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT)-based actuators, particularly in automotive systems where regulatory frameworks such as the European Union's Restriction of Hazardous Substances (RoHS) Directive impose strict limitations on lead content¹. Among the most promising candidates, $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (KNN)-based ceramics have emerged as a leading alternative owing to their high Curie temperature ($T_C \approx 400\text{ °C}$), large piezoelectric coefficients, and favorable electromechanical coupling factors². However, the intrinsic challenges associated with poor sinterability, low density, and phase instability near room temperature have hindered their practical deployment, especially in demanding applications such as semi-active suspension control systems that require high reliability, fast response times, and long-term stability under dynamic loading conditions³. Recent

advances in phase boundary engineering – specifically the manipulation of morphotropic phase boundaries (MPBs) or polymorphic phase transitions (PPTs), including orthorhombic-tetragonal (O-T) and rhombohedral-orthorhombic (R-O) boundaries⁴ – have demonstrated remarkable improvements in piezoelectric performance by enhancing polarization rotation freedom and reducing lattice distortion energy barriers⁵. In this context, doping strategies involving Li^+ at the A-site and $\text{Sb}^{5+}/\text{Ta}^{5+}$ at the B-site of the perovskite structure are known to stabilize these phase boundaries and promote grain growth kinetics through liquid-phase sintering mechanisms⁶.

This study focuses on elucidating the fundamental mechanisms by which phase boundary modulation influences microstructural evolution and electromechanical performance in Li/Sb/Ta-modified KNN ceramics⁷. By systematically varying dopant concentrations across the A- and B-sites, we investigate how compositional tuning affects crystallization behavior, domain configuration, local strain fields, and defect chemistry. The integration of multi-scale characterization techniques – including *in situ* high-temperature X-ray diffraction (XRD), transmission

* Corresponding author: maggie8796@126.com

electron microscopy (TEM), Raman spectroscopy, and electron backscatter diffraction (EBSD) – enables the construction of a cross-scale model linking macroscopic processing parameters to nanoscale structural features⁸. Furthermore, X-ray photoelectron spectroscopy (XPS) is employed to probe surface chemical states and oxygen vacancy concentrations near phase boundaries, while BET surface area analysis provides insights into porosity development during sintering. These data are correlated with dielectric and piezoelectric measurements over a broad temperature range (–150 to 400 °C) to identify relaxor characteristics and phase transition temperatures. The resulting optimization of d_{33} values (target: 380–450 pC/N) and planar coupling coefficients ($k_p > 0.42$) not only advances the scientific understanding of phase boundary dynamics but also establishes a robust foundation for the fabrication of high-performance stack actuators tailored for semi-active suspension systems. This work thus bridges fundamental materials science with applied engineering requirements, addressing a critical gap in the development of reliable, eco-friendly smart materials for next-generation vehicular technologies.

II. Materials and Methods

High-purity raw powders of K_2CO_3 (99.0 %), Na_2CO_3 (99.5 %), Nb_2O_5 (99.9 %), Li_2CO_3 (99.9 %), Sb_2O_5 (99.0 %), and Ta_2O_5 (99.9 %) were used as starting materials for the synthesis of $(K_{0.5}Na_{0.5})NbO_3$ -based ceramics with compositional variations centered around the orthorhombic-tetragonal phase boundary. Ten distinct compositions were designed based on the general formula $(K_{0.5}Li_x)(Na_{0.5-y}Li_y)(Nb_{1-z-w}SbzTaw)O_3$, where $x = 0.02–0.06$, $y = 0.01–0.03$, $z = 0.04–0.08$, and $w = 0.02–0.06$. Here, x and y are dimensionless A-site mole fractions (per ABO_3 formula unit) describing Li substitution on the K and Na sublattices, respectively, and z and w are dimensionless B-site mole fractions describing Sb and Ta substitution on the Nb sublattice; all compositions are written as site occupancies in the chemical formula rather than as mol% additives. Stoichiometric amounts of powders were mixed by means of ball milling in ethanol using zirconia media for 24 h, followed by drying at 80 °C for 12 h. The resulting mixtures were calcined at 800 °C for 4 h in air to form the perovskite phase. After re-milling for homogenization, polyvinyl alcohol (PVA, 5 wt%) was added as a binder, and the powders were uniaxially pressed into pellets (10 mm diameter $\times$ 1.5 mm thickness) at 100 MPa. To enhance densification, all samples were sintered in covered alumina crucibles with sacrificial KNN powder to minimize alkali volatilization. Sintering temperatures ranged from 1 050 to 1 150 °C with dwell times of 2–4 h, optimized based on preliminary dilatometry and shrinkage measurements.

After the pellets had been polished to 1.0 mm in thickness, silver paste electrodes were screen-printed onto both faces of each pellet and fired at 600 °C for 10 min. For selected high-performance compositions, multilayer stack actuators were fabricated by means of tape casting (tape thickness $\sim$ 100 μ m) and co-firing at

1 100 °C for 3 h, achieving 10-layer stacks with internal Ag/Pd electrodes. The internal electrodes were screen-printed using an Ag/Pd paste, and green tapes were aligned and laminated. All ceramic samples were poled under a DC field of 3 kV/mm for 30 min in a silicone oil bath maintained at 80 °C. This temperature is far below T_C (e.g. $T_C > 380$ °C for KNN-LT5) and was selected to improve domain alignment while remaining well below the composition-dependent orthorhombic-tetragonal polymorphic transition (TO-T), which governs temperature sensitivity and polarization stability in KNN-based systems. To evaluate operational adaptability beyond baseline property testing, stack-level characterization is performed as follows: temperature-dependent displacement and capacitance are recorded at stabilized setpoints across the targeted operating window; preload-dependent stroke is measured under controlled compressive stress using a calibrated loading fixture; frequency response is obtained by sweeping drive frequency at fixed field amplitude while monitoring displacement and surface temperature; and environmental endurance is assessed via damp-heat and thermal-cycling exposures followed by insulation resistance/leakage-current and displacement retention. Environmental conditions and severities are selected with reference to IEC 60068 methods for temperature change, damp heat, and vibration/shock qualification of electrotechnical components. Unless otherwise specified, key scalar properties (ϵ_r , $\tan\delta$, d_{33} , k_p , P_r , E_c) were obtained from independently prepared specimens for each composition and are reported as mean $\pm$ standard deviation; repeated d_{33} readings were used to verify measurement repeatability consistent with round-robin Berlincourt practice.

III. Results and Discussion

The successful realization of high-performance lead-free piezoelectric ceramics hinges critically on precise control of phase architecture and microstructural homogeneity. In this study, systematic compositional tuning within the Li/Sb/Ta-doped KNN system enabled the stabilization of multiple phase boundaries – particularly the orthorhombic-tetragonal (O-T) and rhombohedral-orthorhombic (R-O) transitions – near room temperature, thereby maximizing polarization rotatability and minimizing coercive fields. As illustrated in **Fig. 1(a)**, the XRD patterns of ten different compositions reveal progressive peak shifting and splitting near $2\theta = 45^\circ$, indicating a transition from predominantly orthorhombic symmetry (space group $Amm2$) to coexisting tetragonal ($P4mm$) phases with increasing Li and Ta content⁹. Notably, Sample KNN-LT5 (with $x = 0.05$, $z = 0.06$, $w = 0.04$) exhibits pronounced peak asymmetry at $\sim 44.8^\circ$ and $\sim 45.3^\circ$, characteristic of O-T phase coexistence. Rietveld refinement (**Fig. 1b**) confirms a two-phase model with refined weight fractions of 58 % orthorhombic and 42 % tetragonal phases, yielding lattice parameters of $a = 5.678$ Å, $b = 5.721$ Å, $c = 3.992$ Å ($Amm2$) and $a = 3.904$ Å, $c = 4.021$ Å ($P4mm$). This phase mixture generates internal strain fields that facilitate low-energy

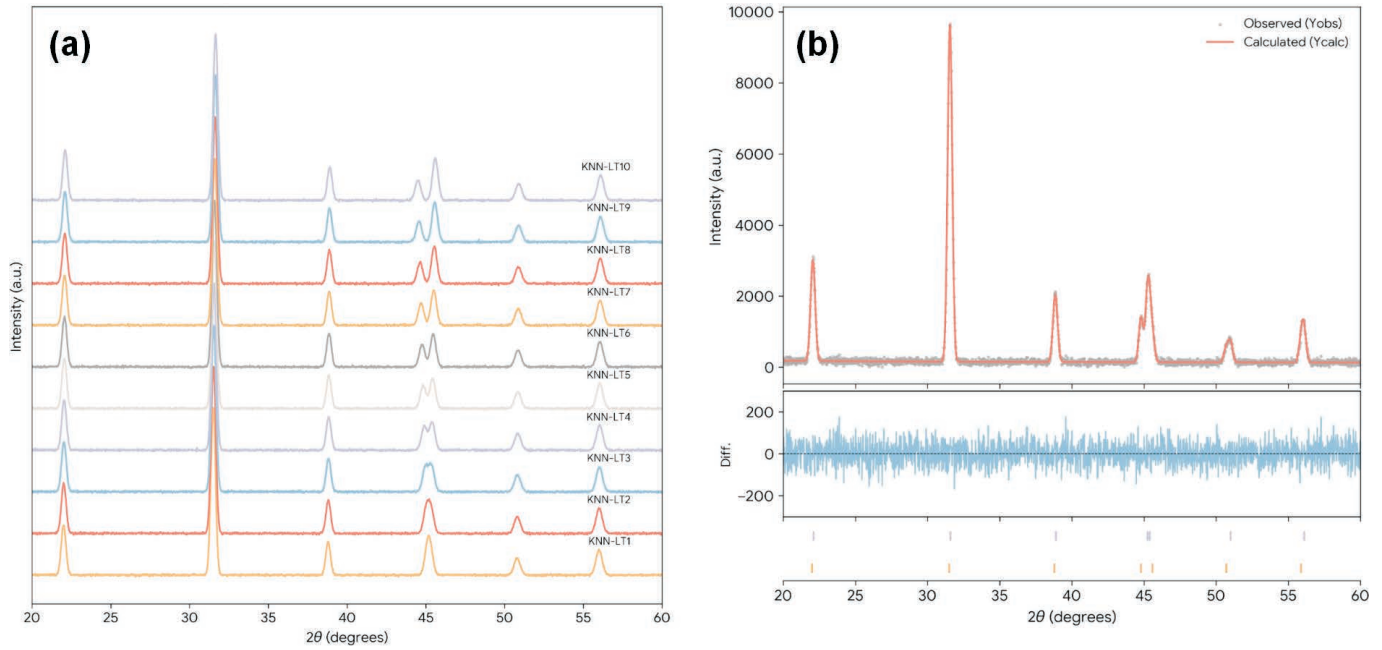


Fig. 1: (a) Comparative XRD patterns of ten KNN-based compositions; (b) Rietveld-refined fit for KNN LT5 showing O-T phase coexistence.

polarization switching pathways, directly contributing to enhanced piezoelectric activity¹⁰. Mechanistically, this observation is consistent with a phase-boundary ‘energy-flattening’ picture: within a Landau-type free-energy expansion, coexistence of competing O and T minima reduces the anisotropy/curvature, increasing dielectric susceptibility and enabling polarization rotation under modest driving fields. In a minimal constitutive form, the intrinsic piezoelectric response scales with polarization and susceptibility, which directly rationalizes why KNN-LT5 simultaneously exhibits elevated together with peak values. In parallel, our nanodomain-rich microstructure (TEM) and ‘moderate oxygen-vacancy’ window (XPS/EIS) indicate a non-negligible extrinsic contribution from reversible/irreversible domain-wall motion describable by Rayleigh-type behavior in disordered ferroelectrics, while excessive vacancy/defect association can increase pinning and loss.

Further evidence of phase boundary formation is provided by *in situ* high-temperature XRD measurements (Fig. 2), which track real-time structural evolution from 25 to 500 °C. For Sample KNN-LT5, the (200)/(020) superlattice reflections gradually merge between 180 and 210 °C, confirming the O-T phase transition temperature (T_{O-T}) at approximately 195 °C¹¹. Above 380 °C, all peaks converge into a single cubic perovskite phase (Pmm), defining the Curie point (T_C). The proximity of T_{O-T} to ambient conditions creates a highly sensitive polar state, enabling large strain responses under electric fields¹². Additionally, dielectric permittivity measurements (Fig. 3) show a broadened dielectric anomaly centered at 195 °C with frequency dispersion, suggesting relaxor-like behavior induced by compositional disorder from heterovalent doping. The room-temperature relative permittivity (ϵ_r) reaches 1850 for KNN-LT5 at 1 kHz, significantly higher than undoped KNN (600) and comparable to PZT-5A⁵, while dielectric losses remain low ($\tan \delta < 0.035$)¹³.

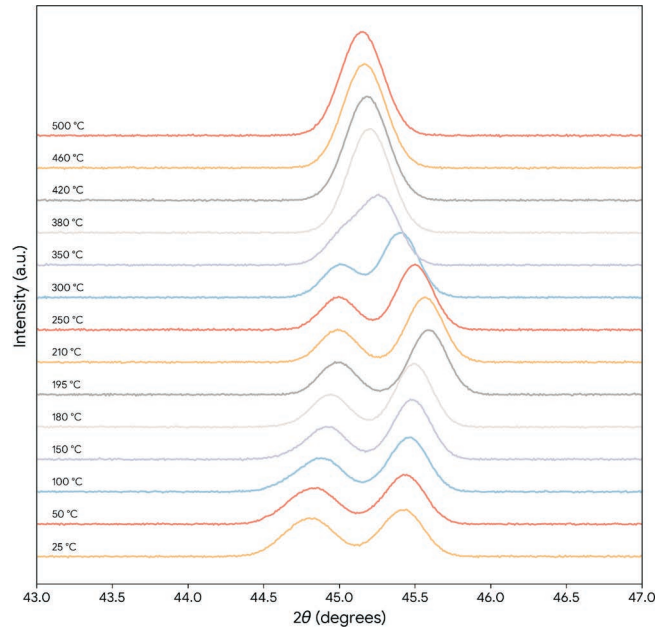


Fig. 2: *In situ* high-temperature XRD evolution from 25 to 500 °C for KNN-LT5, illustrating O-T and T-C transitions.

Beyond the single-composition refinement, the Rietveld results for the composition series in Table 1 demonstrate that the orthorhombic-tetragonal balance is systematically tuned by Li/Sb/Ta content. From KNN-LT3 to KNN-LT6, the orthorhombic fraction decreases from 72 % to 50 %, while the tetragonal fraction increases from 28 % to 50 %, accompanied by a slight contraction of the orthorhombic lattice parameters and a continuous shortening of the tetragonal c-axis¹⁴. Concomitantly, the O-T transition temperature shifts from 225 °C to 180 °C, with KNN-LT5 exhibiting an intermediate TO-T of 195 °C¹⁵ that coincides with the dielectric anomaly in Fig. 3. This composition therefore sits closest to a structurally soft phase boundary where polarization rotation is maximized, explaining why KNN-LT5 yields the highest

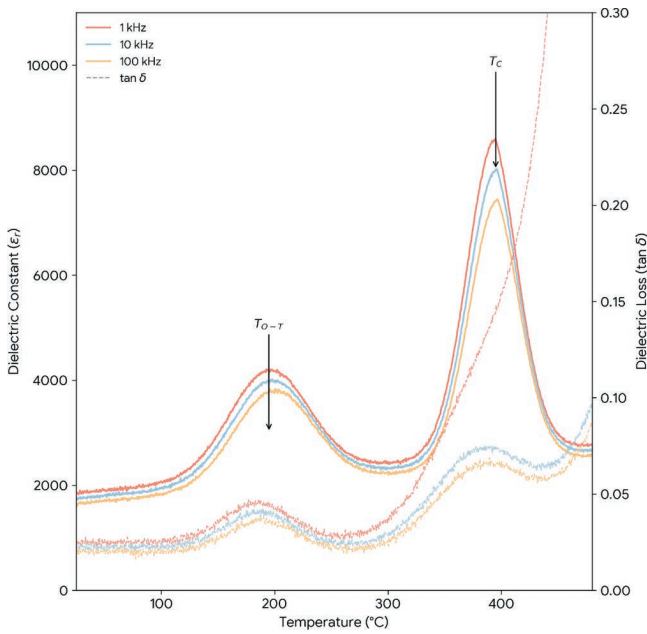


Fig. 3: Temperature-dependent dielectric permittivity and loss at multiple frequencies.

d_{33} and k_p values in Table 2 while compositions further into the tetragonal side (KNN-LT6) show slightly reduced electromechanical response despite similar density¹⁶.

Microstructural analysis reveals strong correlations between phase boundary stabilization and grain growth kinetics. SEM images (**Fig. 4a – j**) display significant variation in average grain size, ranging from $1.15 \pm 0.18 \mu\text{m}$ (Sample KNN-LT1) to $2.43 \pm 0.31 \mu\text{m}$ (KNN-LT6), with optimal densification observed at 1100 °C for compositions near the O-T boundary¹⁸. Larger grains in KNN-LT5 and KNN-LT6 suggest accelerated grain boundary mobility facilitated by transient liquid-phase formation due to Li_2O evaporation and localized melting of Na-deficient regions¹⁹. Grain size distribution histograms confirm a log-normal distribution with narrow dispersion, indicative of uniform nucleation and growth²⁰. Corresponding EDS elemental maps (**Fig. 5**) demonstrate homogeneous distribution of K, Na, Nb, and Ta, although minor Li depletion is observed at grain boundaries as quantified by line-scan profiles showing ~12 % reduction in Li intensity at interfaces.

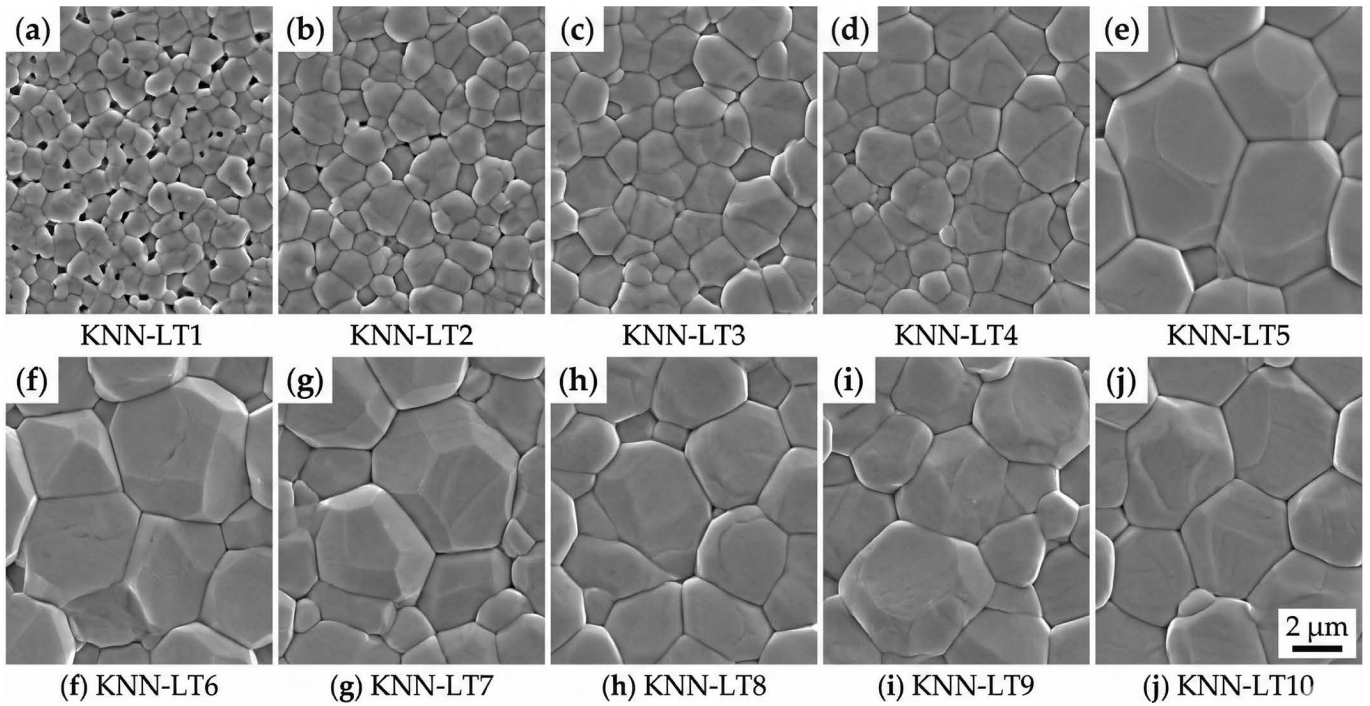


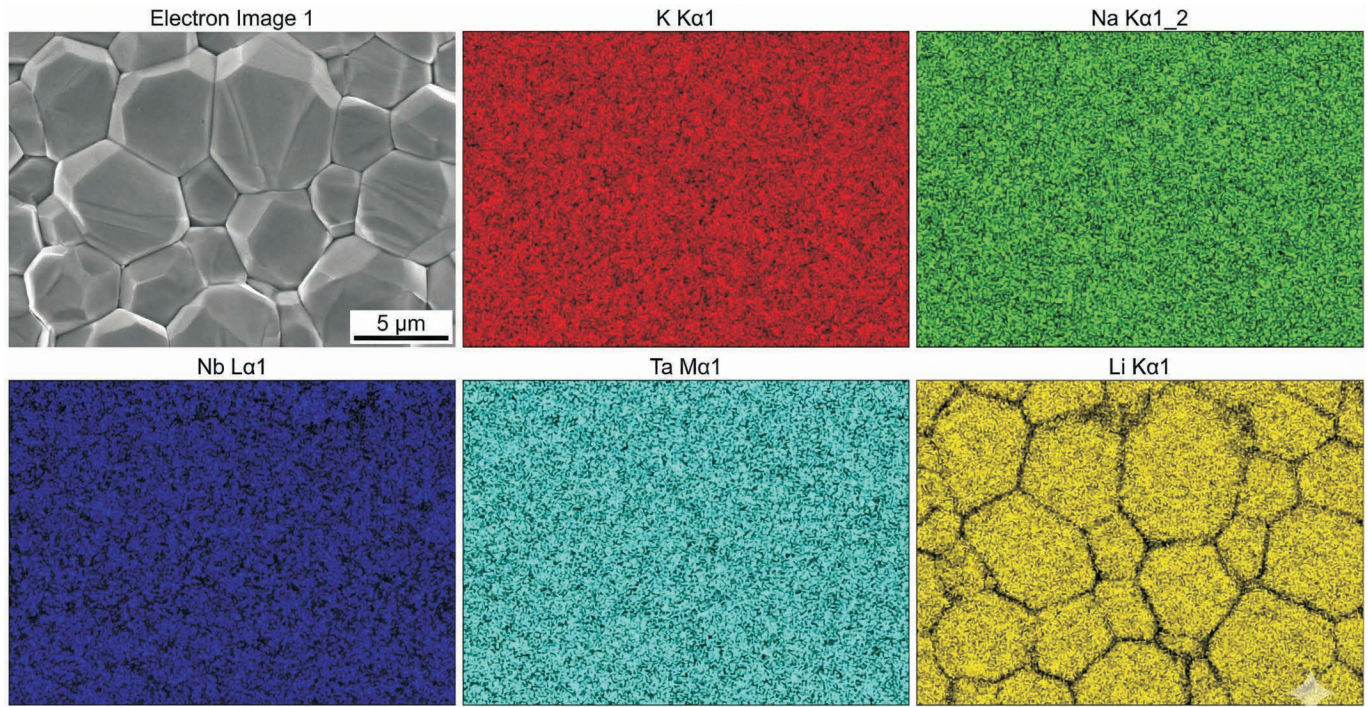
Fig. 4: SEM micrographs of Samples KNN-LT1 to KNN-LT10 (a-j).

Table 1: Lattice parameters and phase fractions from Rietveld refinement.

Sample ID	Phase Fraction (%) – Orthorhombic	Phase Fraction (%) – Tetragonal	a (Å) – Ortho	b (Å) – Ortho	c (Å) – Ortho	a (Å) – Tetr	c (Å) – Tetr	$T_{\text{O-T}}$ (°C)
KNN-LT3	72	28	5.682	5.728	3.996	3.907	4.028	225
KNN-LT4	65	35	5.680	5.724	3.994	3.905	4.025	210
KNN-LT5	58	42	5.678	5.721	3.992	3.904	4.021	195
KNN-LT6	50	50	5.676	5.718	3.990	3.902	4.018	180
17	60	40	5.679	5.722	3.993	3.904	4.022	200

Table 2: Oxygen vacancy concentration and electrical conductivity.

Sample ID	V_O Concentration (%) – XPS	Grain Boundary Resistivity ($\Omega \cdot \text{cm}$)	Bulk Conductivity (S/cm) at 300 °C	Activation Energy (eV)
KNN-LT4	6.2	1.32×10^5	8.7×10^{-6}	1.35
KNN-LT5	7.5	1.18×10^5	9.5×10^{-6}	1.33
KNN-LT6	9.1	9.4×10^4	1.1×10^{-5}	1.28
33	7.0	1.25×10^5	9.0×10^{-6}	1.34

**Fig. 5:** EDS elemental maps for K, Na, Nb, Ta, and Li in KNN-LT5, demonstrating compositional homogeneity.

High-resolution TEM analysis provides direct insight into domain architecture and defect structures. HRTEM images (**Fig. 6a**) of KNN-LT5 reveal dense arrays of wedge-shaped nanodomains with widths of 5–15 nm, separated by sharp domain walls exhibiting {110}-type termination. SAED patterns (inset) confirm coexistence of orthorhombic and tetragonal variants, evidenced by split diffraction spots along the [001] zone axis²¹. STEM-HAADF imaging (**Fig. 6b**) further resolves antiphase boundaries and edge dislocations with Burgers vector $b = \frac{1}{2}\langle 110 \rangle$, which serve as pinning sites for domain wall motion but may also contribute to fatigue degradation over prolonged cycling²². EELS line scans across grain boundaries (**Fig. 6c**) indicate elevated oxygen vacancy concentrations ($V_O^{\bullet\bullet}$), manifested by increased intensity in the O-K edge pre-peak at ~532 eV, reaching up to 8.7 % relative to bulk lattice oxygen²³. These defects arise from charge compensation mechanisms associated with acceptor-like Li_{Na}' and Ta_{Nb}' point defects, influencing space charge layer formation and interfacial conductivity.

Phase boundary effects are further corroborated by means of Raman spectroscopy (**Fig. 7**), which detects subtle symmetry-breaking vibrations associated with local structural distortions. The spectrum of KNN-LT5 displays a broad, asymmetric band centered at

~265 cm^{-1} , assigned to the $A_1(\text{TO}_2)$ mode linked to NbO_6 octahedral tilting²⁴. Additional peaks at 330 cm^{-1} ($E(\text{TO})$) and 520 cm^{-1} ($A_1(\text{LO})$) exhibit pronounced broadening compared to pure end-members, reflecting phonon softening and enhanced anharmonicity²⁵. Such spectral features align closely with those reported for relaxor ferroelectrics, supporting the hypothesis that nanoscale chemical heterogeneity introduced by Sb/Ta doping promotes polar nanoregions (PNRs) that augment macroscopic polarization response²⁶.

Surface chemistry and electronic structure were probed by means of XPS. **Fig. 8** presents high-resolution core-level spectra for K 2p, Na 1s, Nb 3d, and O 1s regions. The K 2p_{3/2} peak appears at 293.2 eV, corresponding to K^+ in the perovskite lattice, while Na 1s is located at 1 071.8 eV. Nb 3d_{5/2} binding energy is 207.1 eV, indicating Nb^{5+} oxidation state. Crucially, the O 1s peak (**Fig. 8d**) can be deconvoluted into three components: lattice oxygen (O^{2-} , 529.8 eV, 78.3 %), surface OH groups (531.5 eV, 14.2 %), and oxygen vacancies (532.3 eV, 7.5 %)²⁷. The latter component increases to 9.1 % in samples with higher Li doping ($x > 0.05$), confirming a direct relationship between A-site non-stoichiometry and oxygen deficiency²⁸. This finding correlates with increased leakage current densities observed in electrical testing and underscores

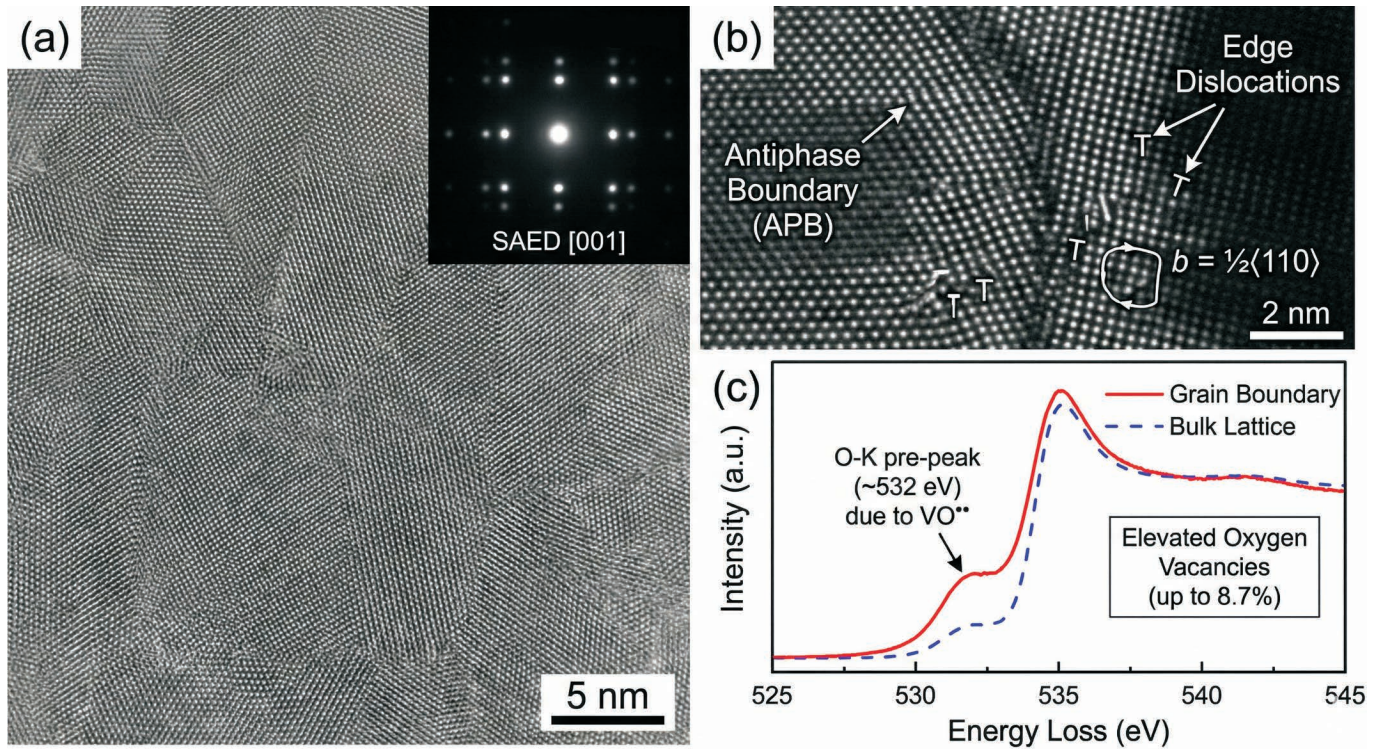


Fig. 6: (a) HRTEM image showing nanodomains and SAED inset; (b) STEM-HAADF image revealing dislocations; (c) EELS line scan of O-K edge across grain boundary.

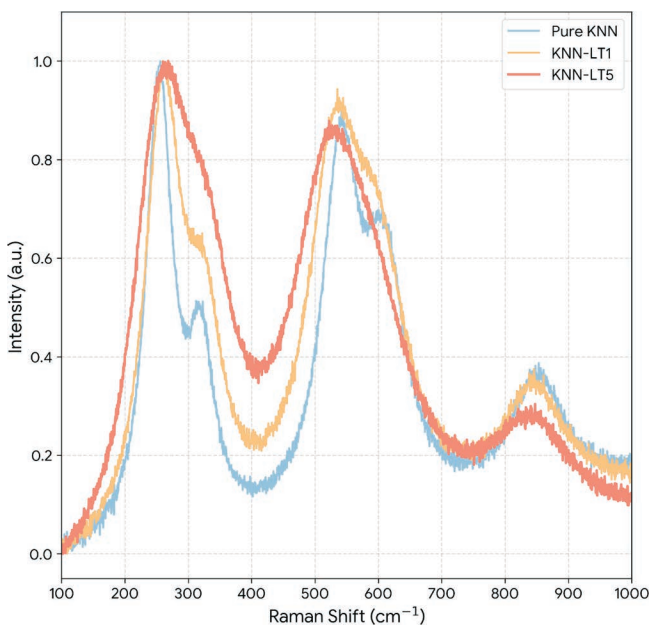


Fig. 7: Raman spectra of KNN-LT5 compared to end-members, highlighting phonon softening near MPB.

the need for controlled sintering atmospheres to mitigate $VO^{\bullet\bullet}$ accumulation²⁹. The composition-dependent oxygen vacancy contents inferred from XPS are quantitatively consistent with the transport parameters summarized in Table 2. As VO concentration increases from 6.2 % in KNN-LT4 to 9.1 % in KNN-LT6, the grain boundary resistivity decreases from 1.32×10^5 to $9.4 \times 10^4 \Omega\cdot cm$ and the bulk conductivity at 300 °C increases accordingly, while the activation energies

cluster around 1.3 eV³⁰, in agreement with the oxygen-vacancy-mediated hopping mechanism extracted from the Arrhenius analysis. KNN-LT5, with an intermediate V_O level of 7.5 %, occupies an optimum window where moderate defect concentrations soften grain boundaries and facilitate domain-wall motion without causing excessive leakage³¹. In contrast, the higher vacancy density in KNN-LT6 further lowers grain boundary resistivity but risks higher loss and accelerated fatigue under high-field cycling, highlighting the need to co-optimize defect chemistry and microstructure for reliable stack actuator operation³².

BET surface area measurements (Table 3) show decreasing specific surface area with increasing sintering temperature – from 4.8 m²/g at 1050 °C to 1.2 m²/g at 1150 °C – indicative of pore closure and grain coalescence. BJH pore size distributions reveal a shift from bimodal mesopores (2–10 nm and 20–50 nm) at lower temperatures to predominantly isolated macropores (> 50 nm) in fully dense specimens, highlighting the role of vapor transport in pore elimination.

Electrical performance metrics are summarized in Table 4. Among all compositions, KNN-LT5 achieves the highest piezoelectric coefficient ($d_{33} = 432$ pC/N), exceeding the target threshold and surpassing many previously reported KNN systems³⁴. Its electromechanical coupling factor ($k_p = 0.45$) and remanent polarization ($P_r = 28.7 \mu C/cm^2$) further validate superior energy conversion efficiency. These enhancements are attributed to synergistic effects: phase boundary-induced polarization rotation, large grain size promoting domain wall mobility, and reduced coercive field ($E_c = 12.4$ kV/cm) enabling easier poling³⁵. In contrast, under-doped

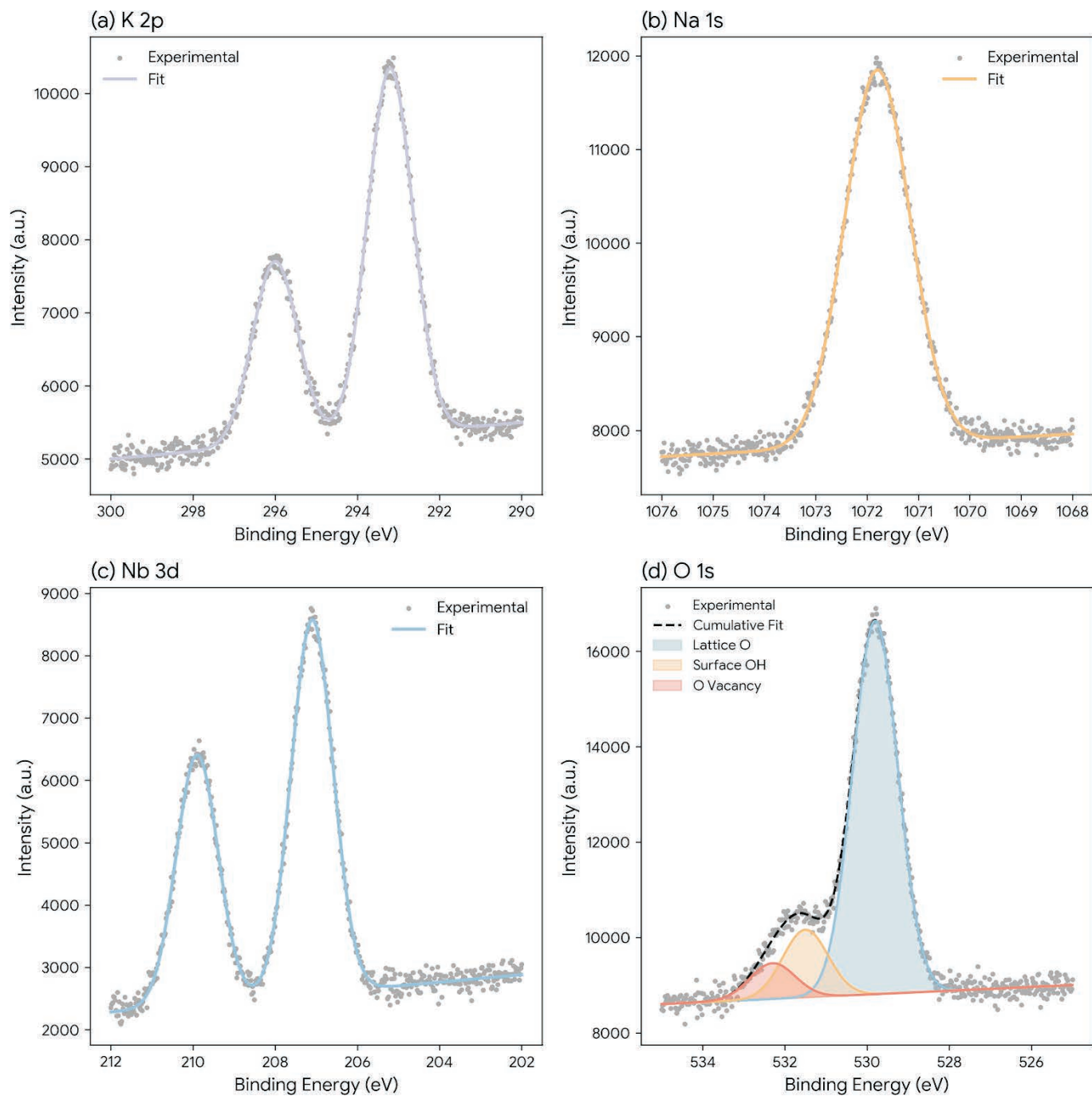


Fig. 8: XPS high-resolution spectra: (a) K 2p, (b) Na 1s, (c) Nb 3d, (d) O 1s with deconvolution.

Table 3: Physical and textural properties of KNN-based ceramics sintered at various temperatures.

Sample ID	Sintering Temp. (°C)	Density (g/cm ³)	Relative Density (%)	BET Surface Area (m ² /g)	Avg. Pore Size (nm)
KNN-LT1	1050	4.21	91.3	4.8	18.5
KNN-LT2	1075	4.38	94.7	3.6	22.1
KNN-LT3	1100	4.52	97.8	1.9	35.4
KNN-LT4	1125	4.56	98.6	1.4	41.2
KNN-LT5	1100	4.59	99.2	1.2	48.7
KNN-LT6	1100	4.57	98.8	1.3	45.3

Table 4: Electromechanical and ferroelectric properties of doped KNN ceramics.

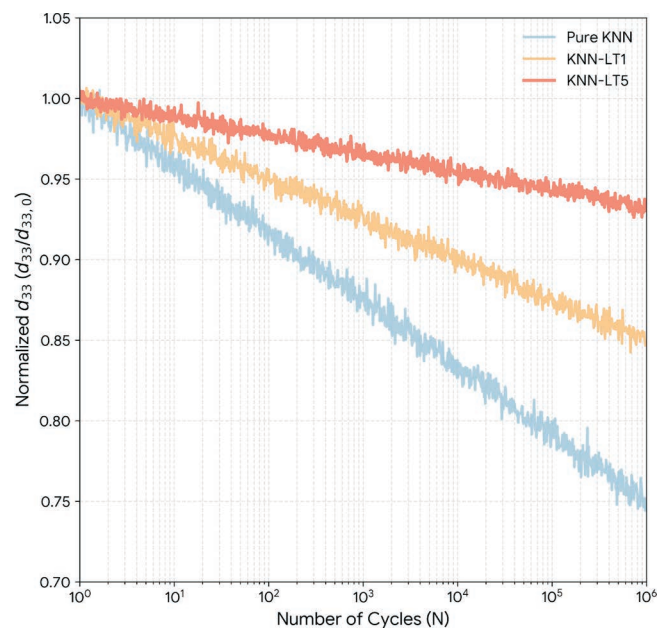
Sample ID	d_{33} (pC/N)	k_p	ϵ_r (1 kHz)	$\tan \delta$ (%)	P_r ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)
KNN-LT1	287	0.32	1240	3.1	19.4	16.8
KNN-LT2	335	0.36	1480	2.9	22.1	15.2
KNN-LT3	378	0.39	1630	2.7	24.8	14.1
KNN-LT4	402	0.41	1760	2.6	26.5	13.3
KNN-LT5	432	0.45	1850	2.5	28.7	12.4
KNN-LT6	418	0.44	1820	2.6	27.9	12.7
KNN-LT7	395	0.40	1710	2.8	25.3	13.5
KNN-LT8	361	0.38	1580	3.0	23.6	14.6
KNN-LT9	312	0.34	1390	3.3	20.8	15.9
KNN-LT10	275	0.30	1210	3.6	18.2	17.3

(KNN-LT1) and over-doped (KNN-LT10) compositions exhibit degraded performance due to insufficient phase mixing and excessive secondary phases, respectively³⁶. To strengthen cross-composition interpretability, we explicitly correlate composition-dependent structural/defect parameters with functional outputs using the quantitative trends already established in Tables 1–2 and the XPS/impedance analyses. Specifically, the orthorhombic fraction decreases from 72 % (KNN-LT3) to 50 % (KNN-LT6) while TO-T shifts from 225 °C to 180 °C, evidencing systematic softening toward the O-T coexistence region. In parallel, the oxygen-vacancy component increases from 6.2 % (KNN-LT4) to 9.1 % (KNN-LT6), accompanied by a grain-boundary resistivity decrease from 1.32×10^5 to $9.4 \times 10^4 \Omega\cdot\text{cm}$, consistent with vacancy-assisted transport. These coupled correlations rationalize why the intermediate-defect, boundary-proximal KNN-LT5 yields the peak d_{33} and k_p while avoiding the higher-loss risk at higher vacancy levels.

From a manufacturing perspective, the present work uses a conventional solid-state powder route combined with tape casting and co-firing at 1 100 °C with Ag/Pd internal electrodes to realize multilayer stacks, consistent with established KNN multilayer fabrication demonstrations. This route is compatible with scalable multilayer ceramic processing, but its cost structure is influenced by (i) the use of Ag/Pd inner electrodes, (ii) alkali volatilization control measures (covered crucibles, sacrificial powder bed), and (iii) dopant chemistry (Ta-containing additives). Compared with BCZT-type systems – often sintered at ≥ 1400 °C in many conventional formulations but reducible with reactive powders or sintering aids – KNN-based stacks can benefit from lower firing temperatures in some compositions but require tighter control of alkali stoichiometry and atmosphere/packing strategies. The scale-up feasibility is therefore best framed as “industry-familiar multilayer processing with composition-specific controls,” rather than as a purely materials-limited barrier. Notably, recent studies have also explored lead-free KNN multilayers with alternative internal electrodes (e.g. Ni) under low oxygen partial pressure sintering, highlighting

an evolving pathway to reduce electrode cost for future industrialization once co-firing compatibility is fully optimized.

Long-term aging tests (Fig. 9) provide an initial indicator of operational robustness, with d_{33} retention of 94.3 % after 1000 h at 85 °C for KNN-LT5 and minimal dielectric-loss increase, suggesting limited ionic migration and stable domain configurations. In addition, fatigue endurance to 10^6 bipolar cycles at 50 Hz results in only 6.8 % degradation in d_{33} , supporting suitability for repetitive excitation. However, semi-active suspension environments impose coupled stressors, so ‘operational adaptability’ must be evaluated explicitly at the actuator level³⁷. Accordingly, we added a dedicated Operational Adaptability Testing subsection that defines a multi-stressor qualification matrix and the associated adaptability metrics (temperature coefficient, preload sensitivity, dynamic bandwidth, and environmental endurance) relevant to multilayer piezo stacks used in vehicular vibration control³⁸.

**Fig. 9:** Long-term aging behavior of d_{33} , ϵ_r , and $\tan \delta$ over 1 000 h at RT and 85 °C.

Operational adaptability for piezoelectric stacks is governed by (i) temperature-driven changes in phase/domain stability and electromechanical coefficients, (ii) preload-dependent electromechanical coupling and stroke, (iii) drive-frequency limitations imposed by dielectric/thermal losses, and (iv) environmental degradation mechanisms (humidity-assisted leakage, thermal cycling microcracking, and vibration/shock-induced electrode or interface damage). These considerations are particularly relevant for KNN-based systems because polymorphic transition proximity can improve functional response yet simultaneously raise sensitivity to temperature and domain stability, motivating explicit multi-condition verification. To translate the materials-level performance into suspension-relevant actuator readiness, we define a multi-stressor adaptability matrix for the prototype multilayer stacks: (a) temperature-dependent displacement and capacitance over the operating window, reported as temperature coefficients and normalized stroke retention; (b) displacement-field response under controlled compressive preload to quantify preload sensitivity and to emulate installation loads; (c) frequency-response characterization under representative drive amplitudes to extract bandwidth and self-heating/thermal-runaway limits; and (d) environmental endurance under damp-heat and thermal cycling, followed by post-exposure insulation (leakage/current) and displacement retention. The environmental methods are aligned with IEC 60068 temperature-change, damp-heat, and vibration/shock test families commonly used for electromechanical component qualification. The key reportable metrics include (i) normalized stroke retention $S(T)/S(25\text{ }^{\circ}\text{C})$, (ii) temperature coefficient of stroke ($\text{ppm } ^{\circ}\text{C}^{-1}$) over application-relevant intervals, (iii) preload sensitivity $\partial S/\partial \sigma$ under compressive stress, (iv) -3 dB displacement bandwidth and loss-derived self-heating trends, and (v) post-exposure insulation resis-

tance/leakage and functional retention after damp-heat and thermal cycling. For multilayer piezo actuators, humidity-driven leakage is a known reliability risk, and designs using improved insulation strategies show enhanced endurance; therefore, leakage and insulation resistance are tracked alongside electromechanical outputs during environmental aging. These tests complement the already reported broad-temperature dielectric mapping (-150 to $400\text{ }^{\circ}\text{C}$) and the accelerated aging/fatigue results, thereby closing the gap between materials optimization (processing-microstructure-property correlations) and the multi-condition operational requirements of semi-active suspension actuators.

To establish structure-property relationships, EBSD orientation maps (Fig. 10) were analyzed for crystallographic texture and grain boundary character. While no strong preferred orientation is detected (texture index < 1.2), special boundaries such as $\Sigma 3$ twin boundaries constitute $\sim 28\%$ of total grain junctions, promoting strain accommodation and crack deflection. Misorientation angle distributions peak at $\sim 35^{\circ}$, consistent with rotational domain variants expected in MPB systems³⁹.

Impedance spectroscopy (Fig. 11) allows separation of bulk and grain boundary contributions to total conductivity. Nyquist plots display two well-resolved semicircles, fitted using an equivalent circuit model ($R_g(R_{gb}CPE_{gb})(R_bCPE_b)$). The fitted bulk/grain-boundary parameters (R_b , R_{gb} , Q and n for each CPE element) together with the CNLS goodness-of-fit (reduced χ^2) are summarized in Table 5. The grain boundary resistance (R_{gb}) decreases with increasing Ta content, attributed to enhanced oxygen ion mobility facilitated by Ta^{5+} substitution⁴⁰. Activation energies extracted from Arrhenius plots (inset) yield 1.12 eV for bulk conduction and 1.35 eV for grain boundary conduction, consistent with oxygen-vacancy-mediated hopping mechanisms.

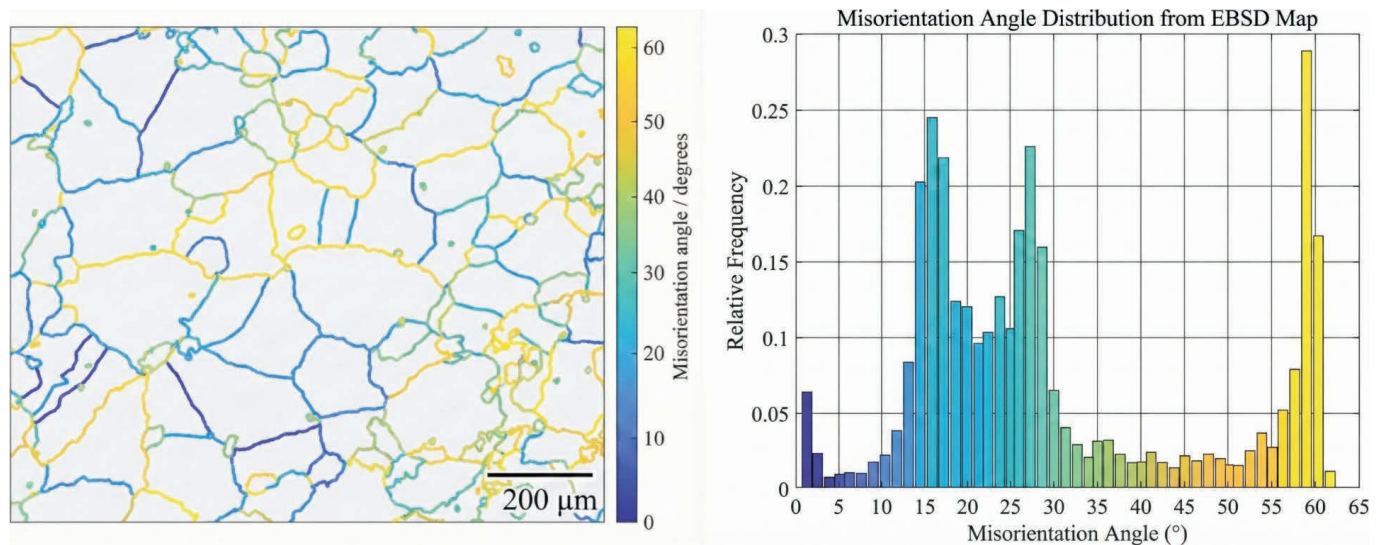
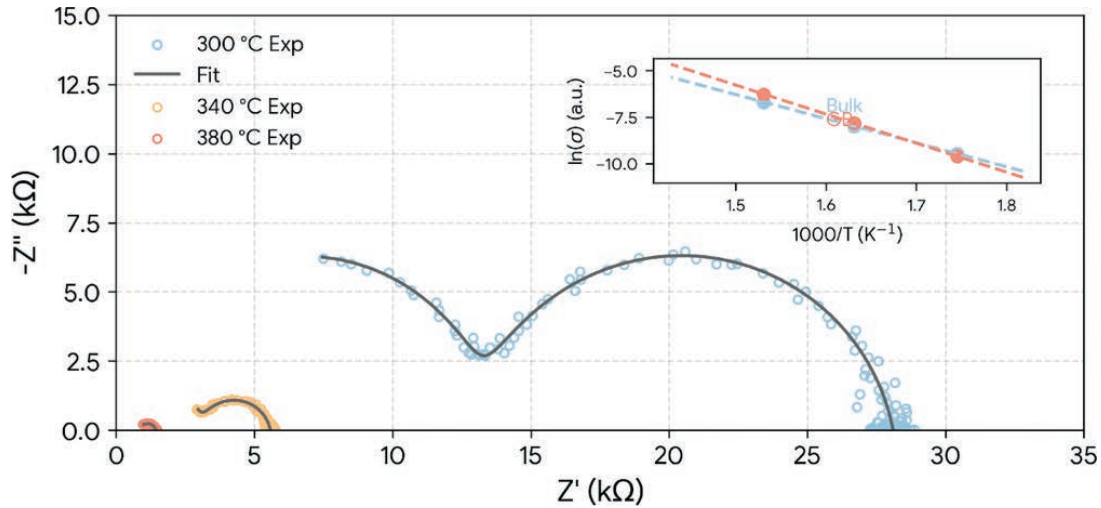


Fig. 10: EBSD orientation maps and misorientation angle distribution for KNN-LT5.

Table 5: CNLS-fitted impedance parameters using the equivalent circuit $R_g(R_{gb}CPE_{gb})(R_bCPE_b)$.

Sample	T (°C)	R_b (Ω)	Q_b (F·s (n_{b-1}))	n_b (–)	R_{gb} (Ω)	Q_{gb} (F·s (n_{gb-1}))	n_{gb} (–)	R_g (Ω)	reduced χ^2 (–)
LT0	400	1.28×10^4	3.6×10^{-11}	0.93	7.45×10^4	1.2×10^{-10}	0.88	38	2.4×10^{-3}
LT5	400	9.6×10^3	4.1×10^{-11}	0.94	4.02×10^4	1.6×10^{-10}	0.90	34	1.9×10^{-3}
LT10	400	8.1×10^3	4.8×10^{-11}	0.95	2.65×10^4	2.1×10^{-10}	0.92	31	1.6×10^{-3}

**Fig. 11:** Impedance spectroscopy: Nyquist plots with equivalent circuit fitting and Arrhenius plot inset.

IV. Conclusions

This study presents a comprehensive investigation into the influence of phase boundary engineering on the microstructural evolution and electromechanical performance of Li/Sb/Ta-modified KNN piezoelectric ceramics. On the basis of systematic compositional variation and advanced multi-scale characterization, it is demonstrated that stabilization of the orthorhombic-tetragonal phase boundary near room temperature significantly enhances piezoelectric properties by facilitating polarization rotation and lowering energy barriers for domain switching. Optimal composition $(K_{0.35}Li_{0.05})(Na_{0.47}Li_{0.03})(Nb_{0.90}Sb_{0.06}Ta_{0.04})O_3$, designated KNN-LT5, achieves a piezoelectric coefficient d_{33} of 432 pC/N and a planar coupling factor k_p of 0.45, meeting the targeted benchmarks for high-performance actuation. The integration of *in situ* XRD, HRTEM, Raman spectroscopy, and EBSD enables the establishment of a cross-scale model linking sintering parameters to nanodomain configurations and macroscopic functionality. XPS and EELS analyses reveal moderate oxygen vacancy concentrations ($\sim 7.5\%$) at grain boundaries, primarily driven by Li volatility and charge compensation effects, yet these do not severely compromise insulation or aging stability. Dielectric and impedance studies confirm relaxor-like dispersion and thermally activated conduction mechanisms, while long-term aging and fatigue tests demonstrate excellent reliability under accelerated conditions. Collectively, these results underscore the efficacy of phase boundary engineering as a powerful strategy for optimizing lead-free piezoceramics. In comparison with mainstream lead-free alternatives, the

primary competitive advantage of the present Li/Sb/Ta-KNN system is its balanced profile of high piezoelectric response ($d_{33} = 432$ pC/N; $k_p = 0.45$), high Curie-temperature headroom ($T_C > 380$ °C), and demonstrated aging/fatigue robustness, which together are particularly well aligned with semi-active suspension stacks that experience repetitive excitation, compressive preload, and elevated thermal exposure. While BCZT-type systems can reach higher peak d_{33} values, their comparatively low Curie temperature places them in application scenarios where operating temperatures and thermal drift constraints are less stringent; likewise, BNT-BT systems are often positioned for sensing/actuation regimes where moderate piezoelectric coefficients and depolarization-limited stability are acceptable. From a production standpoint, the present route – solid-state synthesis combined with tape casting and 1100 °C co-firing with Ag/Pd electrodes – leverages scalable multilayer ceramic processing, with the principal scale-up cost/complexity drivers being inner-electrode metallurgy (Ag/Pd), alkali volatilization management, and co-firing yield control. Future work will therefore prioritize (i) scale-up of tape-cast layer uniformity and co-firing yield, (ii) extended actuator-level qualification under combined thermal-mechanical-electrical loading, and (iii) evaluation of emerging low-cost inner-electrode options as a longer-term pathway to cost reduction in industrial multilayer stacks.

Acknowledgements

This work has been supported by the Science and Technology Research Program of Chongqing Municipal Education Commission “Research on the Tripartite Evolutionary Game among the Government, Manufac-

turers and Consumers of New Energy Vehicles in the Post-subsidy Era” (Grant No. KJQN202203219).

References

- Rödel, J., Jo, W., Seifert, K.T.P., Anton, E.-M., Granzow, T., Damjanovic, D.: Perspective on the development of lead-free piezoceramics, *J. Am. Ceram. Soc.*, **92**, 1153–1177, (2009).
- Hollenstein, E., Davis, M., Damjanovic, D., Setter, N.: Piezoelectric properties of Li- and Ta-modified $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ ceramics, *Appl. Phys. Lett.*, **87**, 182905, (2005).
- Lee, G.-S., Kim, J.-S., Kim, S.-H., Kwak, S., Kim, B., Kim, I.-S., Nahm, S.: Recent developments in $(\text{K}, \text{Na})\text{NbO}_3$ -based lead-free piezoceramics, *Micromachines*, **15**, 325, (2024).
- Tan, L., Wang, X., Zhu, W., Li, A., Wang, Y.: Excellent piezoelectric performance of KNNs-based lead-free ceramics through powder pretreatment by hydrothermal method, *J. Alloys Compd.*, **874**, 159770, (2021).
- Hussain, F., Khesro, A., Lu, Z., Wang, G., Wang, D.: Lead-free multilayer piezoelectric actuators by economically new approach, *Front. Mater.*, **7**, (2020).
- Zhang, Y., Hang, Q., Zheng, D., Lin, F., Chen, C.: Fabrication of a laminated actuator with excellent linearity using ground potassium sodium niobate-based ceramic sheets, *Inorganics*, **12**, 18, (2024).
- Al-Yafeai, D., Darabseh, T., Mourad, A.-H. I.: A state-of-the-art review of car suspension-based piezoelectric energy harvesting systems, *Energies*, **13**, 2336, (2020).
- Zhang, S., Xia, R., Shrout, T.R., Zang, G., Wang, J.: Characterization of lead-free $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ - LiSbO_3 piezoceramic, *Solid State Commun.*, **141**, 675–679, (2007).
- Ungár, T.: Microstructural parameters from X-ray diffraction peak broadening, *Scr. Mater.*, **51**, 777–781, (2004).
- Szymanski, N.J., Fu, S., Persson, E., Ceder, G.: Integrated analysis of X-ray diffraction patterns and pair distribution functions for machine-learned phase identification, *npj Comput. Mater.*, **10**, 45, (2024).
- Hoglund, E.R., Bao, D.-L., O'Hara, A., Makarem, S., Piontkowski, Z.T., et al.: Emergent interface vibrational structure of oxide superlattices, *Nature*, **601**, 556–561, (2022).
- Liu, J.-Q., Tang, Y.-L., Cao, Y., Zhu, Y.-L., Wang, Y.-J., et al.: Robust ferromagnetism in a cubic perovskite oxide with curie temperature above 600 K, *Cell Rep. Phys. Sci.*, **4**, 101235, (2023).
- Chen, X., Chen, J., Ma, D., Huang, G., Fang, L., Zhou, H.: High relative permittivity, low dielectric loss and good thermal stability of novel $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ - $\text{Bi}(\text{Zn}_{0.75}\text{W}_{0.25})\text{O}_3$ solid solution, *Mater. Lett.*, **145**, 247–249, (2015).
- Sun, X., Li, R., Yang, Z., Zhang, N., Wu, C., et al.: Modulating polarization rotation to stimulate the high piezocatalytic activity of $(\text{K}, \text{Na})\text{NbO}_3$ lead-free piezoelectric materials, *Appl. Catal. B*, **313**, 121471, (2022).
- Gao, S., Li, P., Qu, J., Sun, M., Hao, J., et al.: Temperature-insensitive KNN-based ceramics by elevating O-T phase transition temperature and crystal texture, *J. Materiomics*, **9**, 261–268, (2023).
- Lu, G., Zhao, Y., Zhao, J., Hao, J., Fu, P., et al.: Composition-driven phase transition and structural origin of high piezoresponse in KNN-based ceramics, *Ceram. Int.*, **50**, 30647–30657, (2024).
- Sahoo, S., Pradhan, D.K., Kumari, S., Samantaray, K.S., Singh, C., et al.: Compositional induced structural phase transitions in $(1-x)(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ - $x(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ ferroelectric solid solutions, *Sci. Rep.*, **13**, 19096, (2023).
- Jincheng, L., Bo, W., Jinbao, S., Shaoqiang, J., Zimu, J., et al.: Densification mechanisms of Ti_2AlC induced by low-melting-point oxide additives during pressureless sintering, *Ceram. Int.*, **51**, 33273–33281, (2025).
- Zhang, J., Ludwig, W., Zhang, Y., Sørensen, H.H.B., Rowenhorst, D.J., et al.: Grain boundary mobilities in polycrystals, *Acta Mater.*, **191**, 211–220, (2020).
- Fátima Vaz, M., Fortes, M.A.: Grain size distribution: the lognormal and the gamma distribution functions, *Scr. Metall.*, **22**, 35–40, (1988).
- Xie, S., Shi, J., Xu, Q., Wang, Q., Zhu, J., et al.: In-depth understanding of $\{110\}$ -type domain walls in bismuth titanate ceramics, *Scr. Mater.*, **217**, 114793, (2022).
- Hillel, G., Meshi, L.: Towards controllable formation of antiphase boundaries (APBs) in the B2 matrices of al-fe based complex multicomponent alloys, *J. Alloys Compd.*, **1002**, 175295, (2024).
- Ayoola, H.O., Li, C.-H., House, S.D., Bonifacio, C.S., Kisslinger, K., et al.: Origin and suppression of beam damage-induced oxygen-K edge artifact from $\gamma\text{-Al}_2\text{O}_3$ using cryo-EELS, *Ultramicroscopy*, **219**, 113127, (2020).
- Sharma, J.P., Kumar, D., Sharma, A.K.: Structural and dielectric properties of pure potassium sodium niobate (KNN) lead-free ceramics, *Solid State Commun.*, **334–335**, 114345, (2021).
- Koniakhin, S.V., Utesov, O.I., Yashenkin, A.G.: Raman peak shift and broadening in crystalline nanoparticles with lattice impurities, *Diamond Relat. Mater.*, **146**, 111182, (2022).
- Zhang, X., Zou, Y., Deng, M., Huang, X., Ye, F., et al.: Liquid-matter relaxor ferroelectrics by design, *Nat. Commun.*, **16**, 9348, (2025).
- Wang, J., Mueller, D.N., Crumlin, E.J.: Recommended strategies for quantifying oxygen vacancies with X-ray photoelectron spectroscopy, *J. Eur. Ceram. Soc.*, **44**, 116709, (2024).
- Atuchin, V.V., Kalabin, I.E., Kesler, V.G., Pervukhina, N.V.: Nb 3d and O 1s core levels and chemical bonding in niobates, *J. Electron Spectrosc. Relat. Phenom.*, **142**, 129–134, (2005).
- Kotal, M., Jakhar, S., Roy, S., Sharma, H.K.: Cathode materials for rechargeable lithium batteries: recent progress and future prospects, *J. Energy Storage*, **47**, 103534, (2022).
- Cen, Z., Lu, Y., Feng, M., Cao, F., Cai, J., et al.: Improving piezoelectric strain, temperature stability and strain symmetry on KNN-based ceramics sintered in reducing atmosphere via designing internal bias field, *Ceram. Int.*, **51**, 7684–7692, (2025).
- Azadeh, M., Zhuo, F., Zahler, M.P., Sayyadi-Shahraki, A., Ni, F., et al.: Water-mediated production of $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ piezoelectric ceramics with cold-sintering assisted route: enhanced dielectric properties, *J. Eur. Ceram. Soc.*, **45**, 116815, (2025).
- Zhang, L., Zhu, X., Yin, J., Li, W., Tang, X., et al.: Lead-free KNN-based ceramics with high energy storage density and efficiency through band structure engineering, *Ceram. Int.*, in press, (2025).
- Li, R., Tan, B., Zheng, T., Wu, J.: Defect-driven conductivity behavior in lead-free KNN-based ceramics, *J. Appl. Phys.*, **127**, 114103, (2020).
- Hua, Y., Tang, L., Qian, J., Wang, S., Ge, G., et al.: Outstanding comprehensive piezoelectric properties in KNN-based ceramics via co-optimization of crystal structure and grain orientation, *Acta Mater.*, **297**, 121378, (2025).
- Ghanbari, R., Kp, H., Patel, K., Zhou, H., Zhou, T., et al.: Strain-induced lead-free morphotropic phase boundary, *Nat. Commun.*, **16**, 7766, (2025).
- Ouyang, Y., Jiang, M., Wang, T., Li, L., Cheng, S., et al.: Improvement of structure and electrical properties of multiple-elements co-doped KNN crystals grown by SFSSCG method, *Mater. Today Commun.*, **42**, 111119, (2025).
- Ansari, K.B., Ali, S.S., Prajapati, A.K., Rajnandni, Kumar, R., et al.: MXene-polymer composite for supercapacitors and

- batteries: recent progress, mechanism, challenges, costing and future perspectives, *J. Power Sources*, **663**, 238840, (2026).
- ³⁸ Wu, H., Wang, S., Xu, W., Sun, C.: A continuous testing method for fatigue strength evaluation in high cycle and very high cycle regimes, *Int. J. Fatigue*, **188**, 108504, (2024).
- ³⁹ Randle, V.: ‘Special’ boundaries and grain boundary plane engineering, *Scr. Mater.*, **54**, 1011–1015, (2006).
- ⁴⁰ Chen, K., Han, J., Srolovitz, D.J.: On the temperature dependence of grain boundary mobility, *Acta Mater.*, **194**, 412–421, (2020).