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"CRYSTAL GROWTH AND ELECTRICAL CHARACTERIZATION OF LEAD-FREE BCTZ AND KNLSTN PIEZOELECTRIC SINGLE CRYSTALS"

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Abstract: Environmentally benign piezoelectric materials are increasingly being explored as substitutes for conventional lead-based systems such as PZT. Among the promising candidates, Ba(Ca)(Ti,Zr)O (BCTZ) and modified (K,Na)NbO systems containing Li, Ta, and Sb (KNLSTN) demonstrate excellent electromechanical performance, particularly near morphotropic phase boundary (MPB) regions. In the present work, bulk single crystals of BCTZ and KNLSTN were successfully synthesized using the top-seeded solution growth (TSSG) technique. Growth parameters were carefully optimized to obtain crystals with high structural integrity and compositional uniformity. Structural evaluation was carried out using X-ray diffraction, while compositional homogeneity was verified through advanced analytical techniques. Electrical characterization included dielectric response, ferroelectric polarization, and piezoelectric coefficients. The BCTZ system exhibited a composition-driven evolution from relaxor to classical ferroelectric behavior, whereas KNLSTN showed pronounced sensitivity of phase transitions to compositional changes. The obtained results highlight the suitability of these lead-free single crystals for advanced piezoelectric device applications.

Keywords: *Lead-free piezoelectrics, BCTZ, KNLSTN, single crystal growth, TSSG, dielectric response, ferroelectricity*

INTRODUCTION

Piezoelectric materials are widely utilized in modern technologies such as sensing, actuation, and energy harvesting. Conventional systems like Pb(Zr,Ti)O (PZT) possess excellent functional properties; however, the presence of lead raises environmental and health concerns. This has motivated extensive research toward developing lead-free alternatives.

Perovskite-based oxides, including BCTZ and potassium sodium niobate (KNN)-derived systems, have emerged as strong candidates due to their high piezoelectric response. Enhanced properties are often observed near morphotropic phase boundaries, where different crystallographic phases coexist, enabling easier polarization rotation.Single crystals are particularly advantageous compared to polycrystalline ceramics because they eliminate grain boundary effects and provide intrinsic material properties. Therefore, the controlled growth of BCTZ and KNLSTN single crystals is essential for both fundamental understanding and technological applications.

MATERIALS AND METHODS

Raw Materials

- **BCTZ system:** BaCO, CaCO, TiO, ZrO
- **KNLSTN system:** NaCO, KCO, LiCO, NbO, TaO, SbO

Crystal Growth Procedure

Single crystals were prepared using the **top-seeded solution growth (TSSG)** technique, which enables slow and controlled crystallization.

BCTZ Crystal Growth

- Flux: TiO-rich solution
- Temperature range: ~1485–1570 °C
- Seed material: Iridium rod
- Growth controlled through thermal gradients

KNLSTN Crystal Growth

- Flux: LiO–KO-based solvent system
- Growth carried out in a dual-zone furnace
- Platinum wire used for initial nucleation

This approach yielded crystals ranging from millimeter to centimeter scale with good structural

Structural and Chemical Analysis

Structural and compositional characterization was performed using:

- X-ray diffraction (XRD) for phase identification
- Laue diffraction for orientation analysis
- Rietveld refinement for lattice parameter determination
- Electron Probe Microanalysis (EPMA)
- ICP-OES for precise lithium quantification

Electrical Measurements

Dielectric Properties

- Frequency range: 100 Hz to 10 MHz
- Temperature-dependent permittivity measurements

Ferroelectric Characterization

- Polarization–electric field (P–E) hysteresis loops
- Determination of spontaneous polarization

Piezoelectric Measurements

- Resonance–antiresonance technique
- Evaluation of coefficients and coupling factor Samples were electrically poled under fields of approximately 8–10 kV/cm.

RESULTS AND DISCUSSION

Crystal Growth Characteristics

BCTZ crystals were obtained in cylindrical forms exhibiting domain structures, whereas KNLSTN crystals appeared relatively transparent with fewer visible defects. Volatilization of elements such as Ti and Li influenced composition Elemental segregation affected stoichiometry Optimized growth conditions improved uniformity .

STRUCTURAL FEATURES

Both materials exhibited perovskite-type crystal structures:

- **BCTZ:** coexistence of cubic, tetragonal, and rhombohedral phases near MPB
- **KNLSTN:** composition-dependent orthorhombic–tetragonal transitions

Such phase coexistence enhances electromechanical response via polarization rotation.

Dielectric Behaviour

- BCTZ displayed diffuse dielectric maxima indicative of relaxor characteristics
- KNLSTN showed sharp peaks corresponding to structural phase transitions

Temperature-dependent measurements revealed:

- Multiple phase transitions (C–T–R) in BCTZ
- Distinct O–T and T–C transition

Ferroelectric Properties

Well-saturated hysteresis loops confirmed ferroelectric behavior in both systems.

- BCTZ exhibited moderate polarization (~20 μC/cm²)
- KNLSTN showed stronger switching characteristics

A composition-driven transformation from relaxor to normal ferroelectric behavior was observed in BCTZ.

Piezoelectric Performance

- BCTZ crystals demonstrated improved piezoelectric response compared to ceramics
- Typical value: d ≈ 90–100 pC/N
- KNLSTN showed enhanced coefficients near MPB compositions

The absence of grain boundaries in single crystals contributes to superior electromechanical properties.

Composition–Property Correlation

Electrical properties were highly sensitive to slight compositional variations:

- BCTZ: transition from relaxor to ferroelectric state
- KNLSTN: shifts in phase transition temperatures

This emphasizes the importance of precise compositional control during crystal growth.

APPLICATIONS

These lead-free piezoelectric single crystals have potential applications in:

- Sensors and actuators
- Ultrasonic and acoustic devices
- Energy harvesting systems
- Biomedical imaging technologies

Their environmentally friendly nature makes them strong alternatives to lead-based materials.

CONCLUSION

Single crystals of BCTZ and KNLSTN were successfully grown using the TSSG method with good structural quality. Detailed characterization revealed that electrical properties strongly depend on phase structure and composition. BCTZ shows a gradual transition from relaxor to ferroelectric behavior, whereas KNLSTN exhibits sharp phase transitions and high piezoelectric response. These findings confirm their potential for future lead-free piezoelectric technologies.

FUTURE SCOPE

- Enhancement of crystal size and uniformity
- Exploration of dopant effects
- Integration into practical devices
- Development of thin films and nanoscale structures

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