Title	FABRICATION OF LEAD-FREE PIEZOELECTRIC TERNARY CERAMICS SYSTEMS BASED ON BISMUTH SODIUM TITANATE-BISMUTH POTASSIUM TITANATE PREPARED USING THE COMBUSTIONTECHNIQUE
Author	Rattiphorn Sumang
Advisor	Assistant Professor Theerachai Bongkarn, Ph.D.
Co - Advisor	Assistant Professor Thiranee Khumlumlert, Ph.D. Assistant Professor Nipaphat Charoenthai, Ph.D. Sarawut Thountom, Ph.D.
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ABSTRACT

The ternary piezoelectric ceramics systems of $(1-x-y)(Bi_{0.5}Na_{0.5})TiO_3$-$x(Bi_{0.5}K_{0.5})TiO_3$-$yBiFeO_3$,$(1-x-y)(Bi_{0.5}Na_{0.5})TiO_3$-$x(Bi_{0.5}K_{0.5})TiO_3$-$yBi_{0.5}Li_{0.5}TiO_3$ and $(1-x-y)(Bi_{0.5}Na_{0.5})TiO_3$-$x(Bi_{0.5}K_{0.5})TiO_3$-$yK_{0.5}Na_{0.5}NbO_3$ with $0.12\leq x\leq 0.24$; $0\leq y\leq 0.07$, $0.18\leq x\leq 0.26$; $0\leq y\leq 0.12$ and $18\leq x\leq 0.28$; $0\leq y\leq 0.07$, respectively (abbreviated as BNKFT-*x*/*y*, BNKLT-*x*/*y* and BNNKT-*x*/*y*, respectively) were prepared by the combustion technique. Each of systems consists of two main parts. The first part studies the effects of firing temperatures on crystal structure and microstructure of BNKFT-*x*/*y*, BNKLT-*x*/*y* and BNNKT-*x*/*y*ceramics. The second part investigates the effects of *x* and *y*on crystal structure, microstructure and electrical properties of BNKFT-*x*/*y*, BNKLT-*x*/*y* and BNNKT-*x*/*y*ceramics.

First system, BNKFT-0.18/0.03 was calcined from 600 °C to 800 °C for 1-3 h and the sintering temperature ranged from 950 °C to 1050 °C for 1-3 h. The XRD analysis exhibited that the BNKFT powders belonged to a rhombohedral structure. A second phase of $K_4TiO_3O_8$ was detected in the powders calcined below 750 °C. The sintered pellets showed a pure perovskite phase in all samples. The microstructure of BNKFT powders exhibited an almost-spherical morphology and

had a porous agglomerated form. The average particle size and the average grain size of BNKFT powders and ceramics increased with the increase of firing temperatures. The highest densities (ρ = 5.85 g cm^{-3}), maximum dielectric constant (ε_r = 7,850), lowest dielectric loss (tanδ = 0.02) and the maximum piezoelectric coefficient (d_{33} = 213 pC/N) were obtained from a sample sintered at 1050 °C. The optimum calcination and sintering temperature of for samples was found at 750 °C and 1050 °C for 2 h. The variation of x and y content directly effects on crystal structure, microstructure, density, dielectric, ferroelectric and piezoelectric properties of the BNKFT-x/0.03 and BNKFT-0.18/y ceramics. The XRD indicated that the ceramics possess pure single phase of perovskite structure, indicating that K^+ and Fe^+ have diffused into the lattice. With increase in x and y contents, grain size decreases and increase, respectively. The optimum electric properties can be obtained at x = 0.18 and y =0.03, as follows: ρ = 5.85 g/cm^{-3}, ε_r = 7,850, tanδ = 0.02 and d_{33} = 213 pC/N.

Second system, BNKLT-0.20/0.10 was calcined from 600 °C to 850 °C for 2 h and sintered from 900 °C to 1050 °C for 2 h. The XRD diffraction pattern was indexed on the basis of a rhombohedral structure. A second phase of $K_4Ti_3O_8$ and $K_2Ti_6O_3$ was detected in the powders calcined below 750°C. The highest perovskite percentage was observed in the powders calcined above 750 °C. The sintered pellets showed a single phase perovskite in all samples, which indicates that K^+, Bi^+ and Li^+ ions diffuse into BNKLT-0.20/0.10 lattices to form solid solutions.The increase of sintering temperature up to 1025 °C significantly promoted the grain growth and microstructure densification. The T_d of the sample shifted to the higher temperature whereas the T_c shifted to lower temperature regions with increasein sintering temperature. The maximum dielectric permittivity at T_c(ε_r = 4,344), density (ρ = 5.79 g/cm^{-3}) and shrinkage (~18.4%) were obtained from the sample sintered at 1025 °C. The optimum calcination and sintering temperatures of all samples was chosen at 750 °C and 1025°C for 2 h. The effects of x and y contents on structures and electrical properties were examined. The results indicated that the coexistence of rhombohedral (R) and tetragonal (T) phases occur in the system, which tends to evolve into tetragonal symmetry when the x and $y$contents are increased. The diffuseness exponent (γ) of the ceramics was between 1.604 and 1.862, indicating that the BNKLT-x/y solid

solutions exhibited diffuse phase transition behavior. The change in *P-E* loops indicated that the long-range ferroelectric order of the sample was affected and transitioned to the polar nanoregions with increase in x and y contents. The polarization hysteresis loop transitioned from well saturated loops typical of a normal ferroelectric to a pinched loop and then finally to a relaxor state with an increase in x and y contents. The coexistence of polar and non-polar phase at the MPB (BNKLT20/0.03) likely caused the pinching behavior with large strains of ~0.36% (measured at 5 kV/mm) and S_{max}/E_{max} values of~727 pm/V which aresuitable for actuator application.

Third system, BNNKT-0.20/0.03 was calcined from 600 °C to 850 °C for 2 h and sintered from 900 °C to 1050 °C for 2 h. The phase formation and microstructure of samples were examined using X-ray diffraction (XRD) and scanning electron microscope (SEM). The results showed that a single phase of sample was successfully obtained with calcination and sintering temperatures of 750 °C and 1025 °C for 2 h. The structure of ceramics indicated the coexistence of rhombohedral and tetragonal phases, which is consistent with the nature of the specimen with an MPB composition. The increase of sintering temperature significantly encouraged the grain growth and microstructure densification. The maximum density and shrinkage of 5.64 g/cm^3 (95.0 % of theoretical density) and 16.4% at 1025°C were obtained from the sample sintered at 1025 °C. The calcination and sintering temperature of 750 °C and 1025 °C was chosen for fabrication BNNKT-x/yceramics. The structure exhibited co-existing phase between rhombohedral and tetragonal structures with increasing of x content. With increasing of y content, the structure exhibited co-exists phase rhombohedral to pseudo-cubic symmetry. When increased of x and y content, the average grain size decreases from 1.42 μm to 1.02 μm and 1.25 μm to 0.70 μm, respectively. The diffuseness exponent (γ) of ceramics are between 1.817 and 1.939 for composition of x and between 1.766 and 1.999 for composition of $y$indicating that the BNNKT-x/y solid solutions are diffuse phase transition behavior. The change in *P-E* loops of BNNKT-x/y ceramics indicated that the long-rang ferroelectric order of the sample was disturbed and turned to the PNRs with increase of x and y content.

The polarization hysteresis loop transformed from well saturated typical ferroelectric to pinched and then to relaxor state with increase in x and y content.