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Piezoelectric and dielectric characteristics of lead-free BNKLBT ceramic thick film and multilayered piezoelectric actuators

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Abstract

Lead-free piezoelectric 0.885($Bi_{0.5}Na_{0.5}$)TiO_3–0.05($Bi_{0.5}K_{0.5}$)TiO_3–0.015($Bi_{0.5}Li_{0.5}$)TiO_3 0.05$BaTiO_3$ ceramics (abbreviated as BNKLBT-1.5) were prepared by a conventional mixed oxide method. The composition has a piezoelectric d_{33} constant of 154×10^{-12} C/N, an electromechanical coupling coefficient k_t of 0.519, a relatively low dissipation factor (tan δ = 1.6%) at 1 kHz. BNKLBT-1.5 multilayered actuators have been fabricated using a roll-casting technique. Each single layer has dimensions of 9.0 mm × 9.0 mm × 0.2 mm. Four multilayer actuators with 5, 10, 15 and 20 layers have been fabricated. Their capacitance and displacement under an a.c. field were measured. The capacitance measured at 1 kHz is 9.64 nF, 14.69 nF, 25.36 nF, 32.59 nF and the displacement measured at 5 kHz is 867 pm/V, 1331 pm/V, 2060 pm/V, 2442 pm/V, respectively.

Keywords: C. Electrical properties; C. Mechanical properties; D. Perovskites; E. Actuators

1. Introduction

Various types of piezoelectric materials have been studied and used in different related devices since the discovery of piezoelectric effect in 1880 by J. Curie and P. Curie. The most widely used piezoelectric material is lead zirconate titanate, Pb(Zr,Ti)O_3 (PZT)-based ceramics due to their high electromechanical coupling factors and piezoelectric properties. They are commonly used in transducers, sensors and actuators. However, the toxicity of lead oxide and its high vapour pressure during the fabrication of PZT demand alternative environmental friendly materials. In Europe, the legislation on waste electrical electronic equipment has been issued and the use of hazardous substance such as lead in some electrical parts is prohibited from July, 2006. The search for alternative piezoelectric materials is now a very active research topic and a great deal of attention has been focused on $Bi_{0.5}Na_{0.5}TiO_3$ (BNT)-based materials [1–3]. The major raw material for fabricating BNT-based materials is bismuth trioxide. From the Material Safety Data Sheet (MSDS) provided by ChemWatch, bismuth trioxide is a ''Non-hazardous substance. Non-dangerous goods. According to the Criteria of NOHSC, and the ADG Code'' [4], compared with ''Hazardous substance. Dangerous goods According to the Criteria of NOHSC, and the ADG Code'' [5] in lead oxide. BNT-based material can treat as environmental friendliness.

Bismuth sodium titanate, $Bi_{0.5}Na_{0.5}TiO_3$, is a kind of perovskite ferroelectrics discovered by Smolenskii et al. in 1960 [1]. BNT has a relatively large remnant polarization $P_r = 38\ \mu C/cm^2$ and coercive field $E_c = 7.3$ MV/m at room temperature and has a high Curie temperature ($T_c = 320\ ^\circ C$) [2,3]. This material has a high leakage current during poling which caused incomplete poling. The reason for this is the conductivity due to loss of Bi during ceramic processing at high (>100 °C) temperature [6]. In order to improve the performance of BNT-based lead-free piezoelectric ceramics, ($Bi_{0.5}Na_{0.5}$)TiO_3-$BaTiO_3$ [7], ($Bi_{0.5}Na_{0.5}$)TiO_3–($Bi_{0.5}K_{0.5}$)TiO_3 [8], ($Bi_{0.5}Na_{0.5}$)TiO_3–$NaNbO_3$ [9], ($Bi_{0.5}Na_{0.5}$)TiO_3–$BiFeO_3$ [10] and ($Bi_{0.5}Na_{0.5}$)TiO_3–$CaTiO_3$ [11] have been studied. They showed improvement in either easier to pole or have enhanced piezoelectric properties compared with pure BNT ceramics. Rhombohedral (F_R)–tetragagonal (F_T) morphotropic

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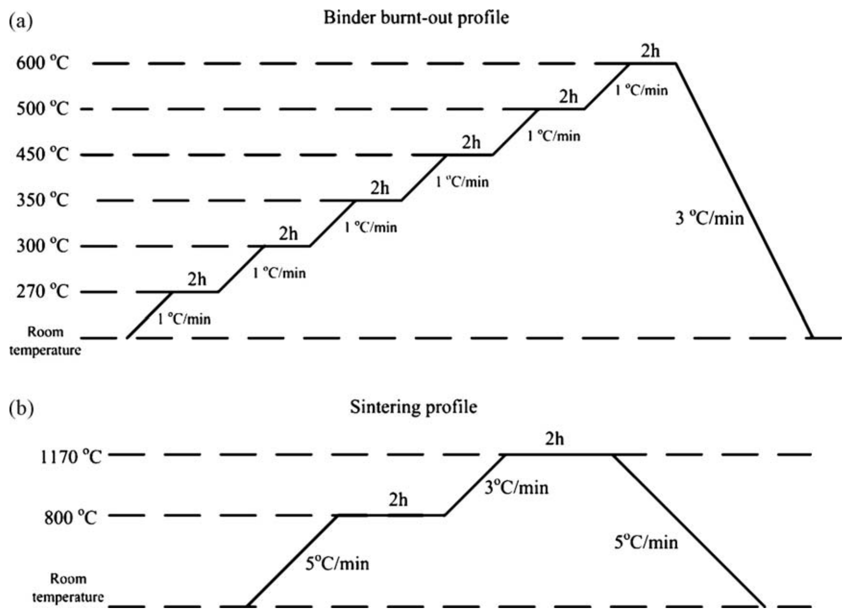

Fig. 1. Temperature profiles during the (a) binder burnt-out process and (b) sintering process of the BNKLBT-1.5 thick film and multilayer actuators.

phase boundary (MPB) can be found in both $(Bi_{0.5}Na_{0.5})TiO_3$–$BaTiO_3$ and $(Bi_{0.5}Na_{0.5})TiO_3$–$(Bi_{0.5}K_{0.5})TiO_3$ systems [7,8] and the ceramics have relatively high piezoelectric and dielectric properties at compositions near the MPB. Multicomponent systems such as combinations of $(Bi_{0.5}Na_{0.5})TiO_3$–$(Bi_{0.5}K_{0.5})$-TiO_3–$BaTiO_3$ are effective in improving the piezoelectric properties. Nagata et al. firstly reported the piezoelectric properties of some compositions in the $(Bi_{0.5}Na_{0.5})TiO_3$–$(Bi_{0.5}K_{0.5})TiO_3$–$BaTiO_3$ (BNKBT) system which have substantial property enhancement [12] and Wang et al. [13,14] reported detail information of the BNKBT system including the dielectric, piezoelectric and ferroelectric properties as well as the variation in depolarization temperature (T_d). We have reported the modified BNKBT with $(Bi_{0.5}Li_{0.5})TiO_3$ as dopant and the composition $0.885(Bi_{0.5}Na_{0.5})TiO_3$–$0.05(Bi_{0.5}K_{0.5})TiO_3$–$0.015(Bi_{0.5}Li_{0.5})TiO_3$–$0.05BaTiO_3$ ceramics (abbreviated as BNKL BT-1.5) has good performance in overall properties [15]. Different devices have been fabricated and their properties are comparable to devices based on PZT [15–18]. In this study, we have fabricated BNKLBT-1-5 ceramics thick films by a roll-casting technique. Actuators with different numbers of ceramic layers are fabricated. The dielectric and piezoelectric properties of the actuators are measured and reported.

2. Experimental procedures

BNKLBT-1.5 composition was prepared by a conventional mixed oxide technique using commercially available reagent grade metal oxides or carbonate powders. The powders were weighed and mixed well in alcohol using zirconia balls for 10 h. The calcination was conducted at 800 °C for 2 h. After calcinations, the mixture was milled again in alcohol for 10 h.

Polyvinyl alcohol solution (PVA, 20 wt% solution) and the milled powder with weight ratio of 4:1 were mixed to form a slurry and was used in roll-casting to form ceramic thick films with 220 μm in thickness. Green sheets were then cut into 10 mm × 10 mm squares. Pt/Ag (20/80) electrode was painted onto the surfaces with rectangular shape (6 mm × 8 mm) as internal electrodes using a screen-printing technique. Electroded ceramic sheets were stacked and laminated inside a compression mould and subjected to hot pressing at 150 °C under a pressure of 20 kN/cm^2 for an hour. As the green ceramic sheets contained large amounts of organic substances, they gave rise to rapid gas evolutions during the binder burnout process. The binder burnout temperature profile (as shown in Fig. 1(a)) was determined based on the result of thermal gravimetric analysis (TGA). Because the Bi loss is a key factor in the understanding of the properties of ceramics in this system and because this result is behind the thermal treatment used, the TGA curve must be provided to show the different steps in the thermal evolution of the green bodies. A relatively low heating rate (1 °C/min) was used. The sample was sintered at 1170 °C for 2 h (refer to Fig. 1(b) for temperature profile). The sample was poled under a d.c. electric field of 4.0 kV/mm for 15 min in silicone oil at room temperature.

Ferroelectric P–E hysteresis loops of a single ceramic sheet were measured using a standard Sawyer–Tower circuit at 100 Hz. The dielectric and piezoelectric properties were measured using an impedance analyzer (Agilent 4294A). The piezoelectric d_{33} coefficient was measured by a d_{33} meter (Beijing Institute of Acoustics, model ZJ-3B). The displacements of the multilayer actuators were measured using a Polytec OFV 3001 laser vibrometer and the setup is shown in Fig. 2.

3. Results and discussion

The ferroelectric P–E loops of the BNKLBT-1.5 bulk ceramic and a single ceramic sheet are shown in Fig. 3. The remnant polarization (P_r) of the sheet is about 31.0 μC/cm^2,

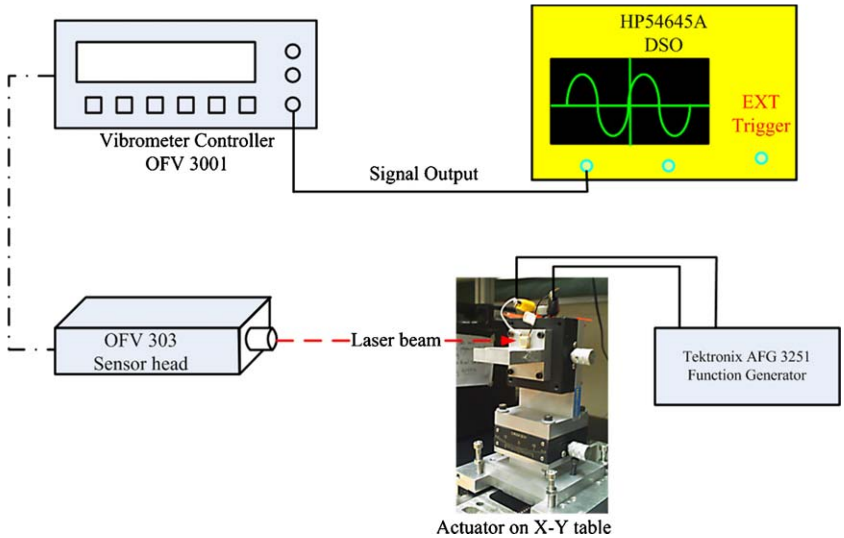

Fig. 2. Schematic diagram of the displacement measurement using laser vibrometer.

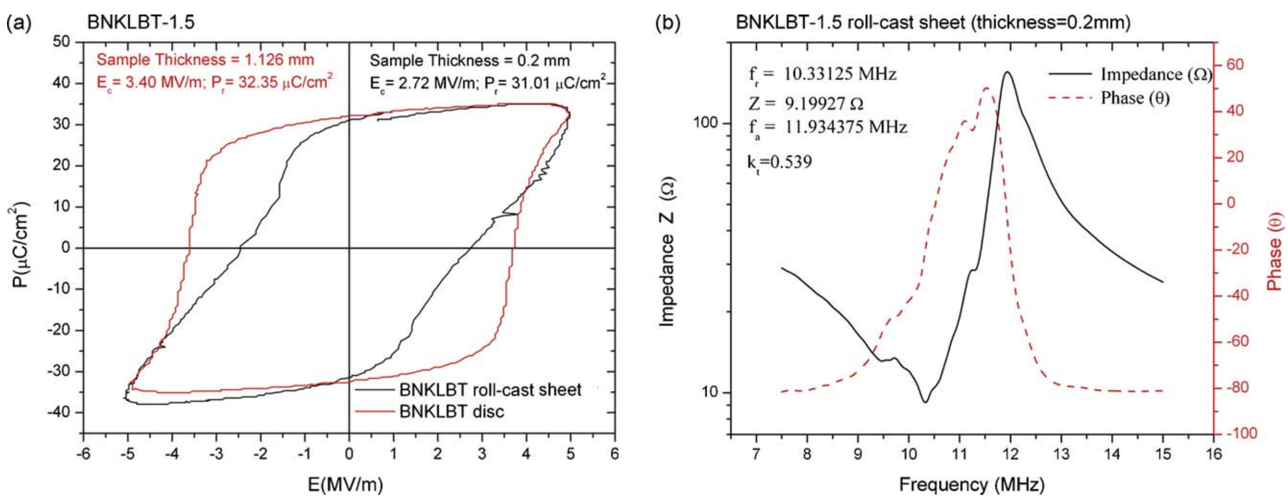

Fig. 3. (a) Ferroelectric *P–E* loop measurement result of ceramic sheet and ceramic disc and (b) the impedance-phase frequency spectrum of a ceramic sheet.

which is comparable with the bulk ceramic sample ($P_r \sim 32.4\ \mu C/cm^2$). The coercive field ($E_c = 2.7$ MV/m) of the ceramic thick film is lower than that of the ceramics disc ($E_c = 3.40$ MV/m). Fig. 3(b) is the impedance and phase versus frequency spectra of the single ceramic sheet. The performance of the ceramic thick film was characterized by a resonance technique. With the measured resonance and anti-resonance frequency of the specified vibration modes, the ceramic properties can be evaluated. The thickness resonant mode of the sheet is found at ∼10.3 MHz and a sharp and pure impedance/phase frequency spectrum is obtained. The electromechanical coupling factor in thickness mode (k_t) is evaluated. The capacitance and dielectric loss were measured at 1 kHz. With these data and other parameters, the material parameters of the BNKLBT sheet are determined. The results are compared with the bulk sample and shown in Table 1. It is seen that the properties of the roll-cast BNKLBT thick film are comparable with those of the BNKLBT bulk sample.

Fig. 4 shows the schematic diagrams and photograph of multilayered actuators with 5, 10, 15 and 20 layers, respectively. The capacitance–frequency responses of the samples under unpoled and poled conditions are shown in Fig. 5. Resonance peaks are found in poled samples at ∼300 kHz which is the length-extension mode of the sample.

Table 1
The properties of BNKLBT ceramic sheet and ceramic disc.

Parameters	Ceramic disc	Ceramic thick film
Density (kg/m^3)	5800	5784
E_c (MV/m)	3.4	2.7
P_r (μC/cm^2)	32.4	31.0
d_{33} (pm/V)	154.7	150.3
ε_{33} at 1 kHz	684.3	731.2
tan δ (%) at 1 kHz	1.67	3.5
k-factor	$k_t = 0.519$ $k_p = 0.309$	$k_t = 0.539$

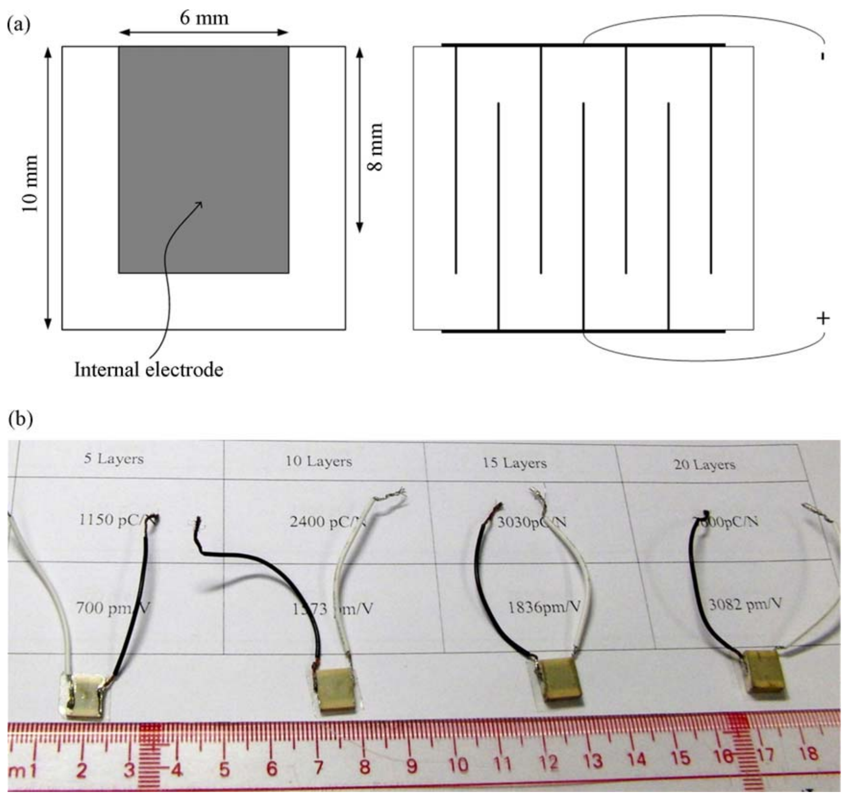

Fig. 4. (a) Schematic diagrams and (b) photographs of multilayer actuators with different layers of ceramic sheets.

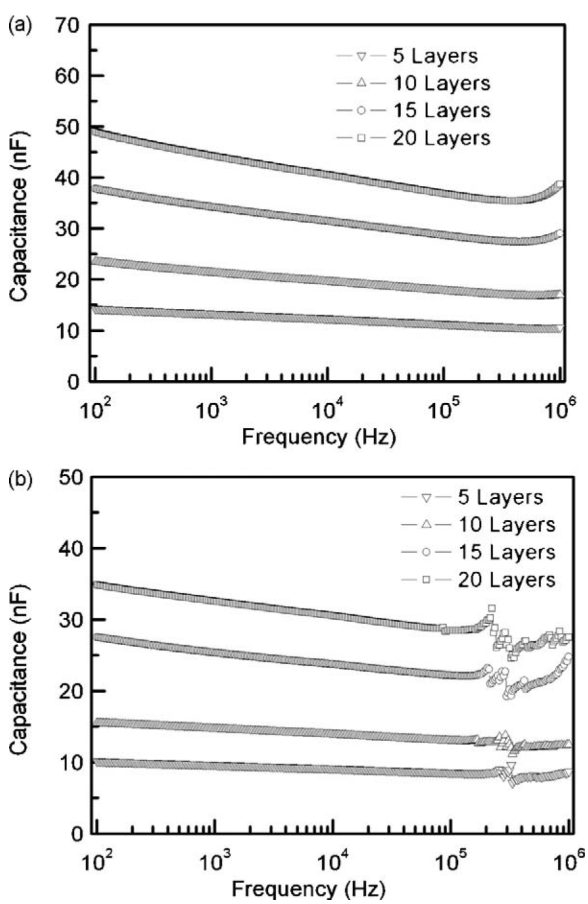

Fig. 5. The capacitance–frequency spectrum of (a) unpoled multilayer samples and (b) poled multilayer samples.

Displacement of the multilayer actuators were measured using a laser vibrometer under different driving voltages. The effective piezoelectric coefficient of the multilayered actuator was calculated by dividing the measured displacement of the actuator by the corresponding driving voltage. The frequency responses of the actuators were investigated by using a fixed driving voltage (20 V_{p-p}) of various frequencies, ranging from 1 kHz to 15 kHz with a step size of 1 kHz, and results are shown in Fig. 6. All the actuators have a rather linear frequency response at frequencies below 5 kHz and the averaged effective piezoelectric coefficient of the 5, 10, 15 and 20 layers multilayered actuators are 670 pm/V, 1345 pm/V, 1865 pm/V and 2930 pm/V, respectively. As d_{33} of each layer of ceramic film is ~150 pm/V and the films are connected electrically in parallel, the calculated d_{33} of the multilayers are 750 pm/V, 1500 pm/V, 2250 pm/V and 3000 pm/V. These are in reasonable agreement with the measured values.

Fig. 7 shows displacement characteristics of the BNKLBT multilayered actuators under different driving voltages (0–20 V_{p-p}, step size of 2 V) with 5 kHz and 10 kHz operation frequencies, respectively. The measured results are presented as symbols and data were linearly fitted and the fitted lines are shown in dashed lines. All the actuators have good linearity with respect to the driving voltage. The slope of the linearly fitted curve is representing the effective piezoelectric coefficient of the actuator. All the calculated data are summarised in Table 2. The 20-layered actuator has the highest effective piezoelectric coefficient under different operation frequencies and the value is nearly double that of the value of the 10-layered actuator in most of the measurement. This shows that the 20-

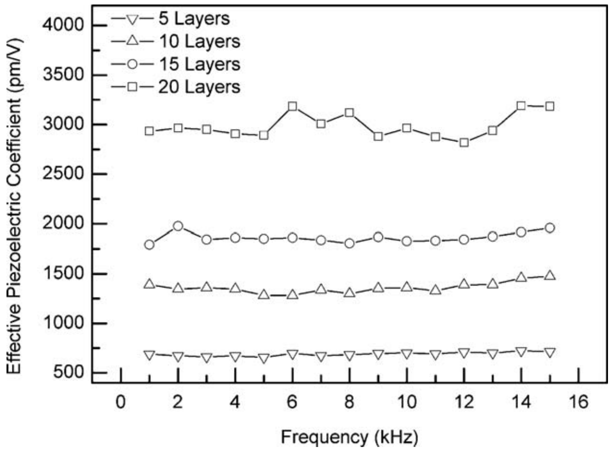

Fig. 6. The frequency response of multilayer actuator displacement output under 20 V_{p-p} driving voltage, 5-layers; 10-layers, 15-layers and 20-layers, respectively.

Table 2
Summary of effective piezoelectric coefficients of lead-free BNKLBT multi-layer actuators.

Effective piezoelectric coefficient	5-layers	10-layers	15-layers	20-layers
Under 5 kHz excitation (pm/V)	867	1331	2060	2442
Under 10 kHz excitation (pm/V)	700	1573	1836	3082
Under d_{33} meter (100 Hz) excitation (pm/V)	1150	2400	3030	3600
Average over 1–15 kHz (pm/V)	670	1345	1865	2930
Calculated d_{33} (pm/V)	750	1500	2250	3000
Capacitance measured at 1 kHz (nF)	9.64	14.69	25.36	32.59
Dielectric loss measured at 1 kHz (%)	2.97	3.35	3.39	3.60

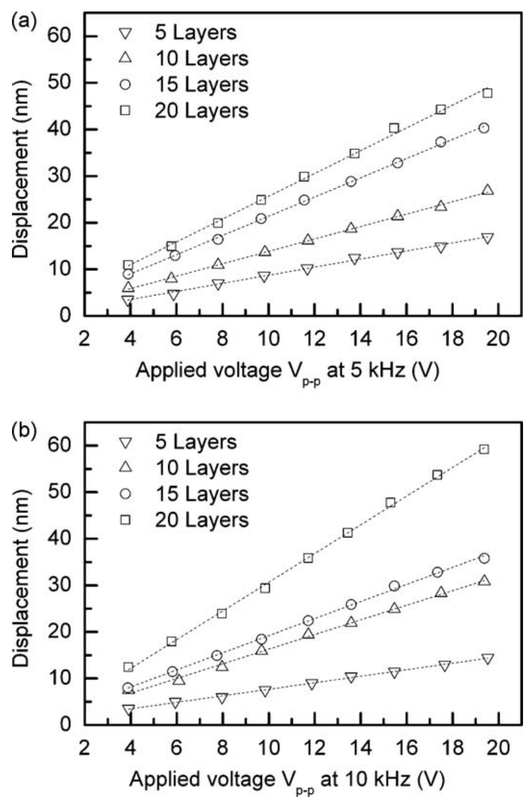

Fig. 7. The displacement characteristic of BNKLBT multilayer actuators under different driving voltage at (a) 5 kHz and (b) 10 kHz.

layered actuator is well fabricated without de-lamination between layers. The lead-free multilayer actuator with good linearity in both frequency response and voltage response, relatively high displacement output has the potential to be used as actuators in a wire-clamp in microelectronic packaging industry or other applications.

4. Conclusion

In summary, $0.885(Bi_{0.5}Na_{0.5})TiO_3$–$0.05(Bi_{0.5}K_{0.5})TiO_3$–$0.015(Bi_{0.5}Li_{0.5})TiO_3$–$0.05BaTiO_3$ ceramics (abbreviated as BNKLBT-1.5) ceramic thick films have been prepared successfully using a roll-casting technique. The dielectric, piezoelectric and ferroelectric properties of the ceramic thick films have been measured and the results are comparable with those of bulk BNKLBT-1.5 ceramic disc. The ceramic thick films are used to fabricate multilayered actuators with different number of ceramic layers including 5, 10, 15 and 20 layers, respectively. The actuators are excited by an a.c. signal and the corresponding output displacements were measured by a laser vibrometer. Results shown that the lead-free BNKLBT multilayer actuators have good linearity in both frequency response and voltage response, relatively high displacement output. They are potential candidate for actuators in various industrial applications.

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