Study of BNKLBT-1.5 lead-free ceramic/epoxy 1-3 composites

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Bismuth sodium titanate based lead-free ceramic fiber with the chemical formula of $0.885(Bi_{0.5}Na_{0.5})TiO_3-0.05(Bi_{0.5}K_{0.5})TiO_3-0.015(Bi_{0.5}Li_{0.5})TiO_3-0.05BaTiO_3$, BNKLBT-1.5, has been fabricated by a powder-based extrusion method. The ceramic fibers with 400 μm diameter were well crystallized after being calcined at 800 °C and sintered at 1170 °C. The piezoelectric and ferroelectric properties of the single fiber were found to be 155 pC/N and ~34.5 $\mu C/cm^2$, respectively, which is comparable with that in bulk sample. 1-3 ceramic/polymer composites were fabricated by two routes, including dice and filled method and fiber pick-and-place method. Theoretical models were used to calculate the piezoelectric properties of the composites and compared with experimental results. © *2007 American Institute of Physics*.
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INTRODUCTION

Lead zirconate titanate [$Pb(Zr,Ti)O_3$, abbreviated as PZT] ceramics are commonly used piezoelectric materials due to their superior piezoelectric properties. However, the high PbO vaporization and contamination during processing and disposal cause a crucial environmental pollution. For this reason, it is desirable to use lead-free piezoelectric ceramics to replace PZT in the near future. 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.

It is known that bismuth sodium titanate $(Bi_{1/2}Na_{1/2})TiO_3$ composition (BNT) is one type of important lead-free ceramics with perovskite structure discovered by Smolenskii *et al.* in 1960s.[1] At room temperature, BNT has a relatively large remnant polarization $P_r=38\ \mu C/cm^2$ and a high coercive field $E_c=7.3$ MV/m. It also has a high Curie temperature ($T_C=320$ °C).[2,3] However, this material has a high leakage current during poling which caused incomplete poling. In order to improve the performance of BNT-based lead-free piezoelectric ceramics, different dopings in BNT-based system have been used, including $BaTiO_3$, $Bi_{0.5}K_{0.5}TiO_3$, $NaNbO_3$, $Ba(Cu_{0.5}W_{0.5})O_3$, etc.[4–8] The modified BNT ceramics showed improvement in either easier to pole or have enhanced piezoelectric properties compared to pure BNT ceramics. Based on the finding of those binary systems, multicomponent systems were developed and it was found that the properties of BNT can be further enhanced. $(Bi_{0.5}Na_{0.5})TiO_3-(Bi_{0.5}K_{0.5})TiO_3-BaTiO_3$ (BNKBT) is a system which is firstly reported by Nagata *et al.*[8] In our previous work, $0.90(Bi_{0.5}Na_{0.5})TiO_3-0.05(Bi_{0.5}K_{0.5})TiO_3-0.05BaTiO_3$ (BNKBT-5) was found to have good performance in overall properties.[9,10] In another similar system, the $(1-x)(Bi_{0.5}Na_{0.5})TiO_3-x(Bi_{0.5}K_{0.5})TiO_3$ system, the piezoelectric d_{33} constant, and electromechanical planar coupling factor k_p were enhanced by doping small amount of lithium ions to form $(Bi_{0.5}Li_{0.5})TiO_3$ (BLT) in the system.[11–13] The properties of $(0.90-x)(Bi_{0.5}Na_{0.5})TiO_3-0.05(Bi_{0.5}K_{0.5})TiO_3-x(Bi_{0.5}Li_{0.5})TiO_3-0.05BaTiO_3$ ceramics (abbreviated as BNKLBT-100x, with x ranged from 0 to 2.5 mol %) system have been investigated. Variations of the electrical properties and structures with the amount of BLT have been examined. It was found the BNKLBT-1.5 has good piezoelectric and dielectric properties which is a potential candidate for different device applications.[14,15]

In this study, BNKLBT ceramics were fabricated in fiber form using a powder-based extrusion method and in disk form using a conventional metal oxide mixing method. BNKLBT/epoxy 1-3 composites with different volume fractions were then fabricated by a dice-and-fill (DF) method (using BNKLBT disks) and a fiber-pick-and-place (FP) method (using BNKLBT fibers). Theoretical model was used to calculate piezoelectric properties of the composites and compared with the experimental results.

EXPERIMENTAL PROCEDURE

A conventional mixed oxide technique was used to prepare the BNKLBT-1.5 ceramic powder. Reagent grade Bi_2O_3, Na_2CO_3, $BaCO_3$, K_2CO_3, Li_2CO_3, and TiO_2 were used as the raw materials. They were weighed according to the formula $0.885(Bi_{0.5}Na_{0.5})TiO_3-0.05(Bi_{0.5}K_{0.5})TiO_3-0.015(Bi_{0.5}Li_{0.5})TiO_3-0.05BaTiO_3$. The powder was ball milled for 10 h in ethanol using zirconia balls. Calcination was conducted at 800 °C for 2 h. The powder was then ball milled together with ethanol for 10 h to obtain powder with particle size around 1–3 μm. For ceramic disks, polyvinyl alcohol solution (PVA 5 wt %) was added into the powder as binders after drying the powder. They were well mixed and pressed in disk shape. The disk samples were then sintered at 1170 °C for 2 h in air. The final dimensions of the disks are 10 mm in diameter and 1.3 mm thick.

BNKLBT green fibers were extruded using slurry formed by mixing presintered BNKLBT powder with suitable amounts of binder. Poly(acrylic acid) (25% aqueous so-

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lution) was dissolved in water to form a binder solution. The powder to binder solution ratio was 1: 0.2. Then the mixture was stirred using a magnetic stirrer until it became a uniform slurry. The slurry was poured into a metal spinnerette and placed into a fiber extrusion machine equipped with a heater. After the slurry has been densified in the spinnerette at 65 °C for 15 min, the fiber was extruded using a gel-spun fiber machine (OneShot III from Alex James & Assoc., Inc). The spinnerette was equipped with a die of 500 μm pinhole. The fibers were collected on a spindle. Diameter of the green fibers was ~450 μm.

Since the green fibers contain high organic contents, removal of the organics usually results in a large shrinkage and cracking of the fibers. In order to prevent fiber cracking, the heating procedure and atmosphere should be adjusted. Guided by the thermogravimetric analysis (TGA) profile of the green fibers, a slow heating rate of 0.5 °C/min in reducing atmosphere (CO) during pyrolysis was used to avoid fiber cracking. The pyrolyzed fibers were subsequently sintered at 1170 °C for 2 h to obtain dense and crack-free BNKLBT ceramic fibers. The diameter of the sintered fiber was about 400 μm.

The microstructure of the ceramic fibers was studied by a scanning electron microscope (Leica Stereoscan 440). The *P-E* hysteresis loops of the disks and fibers were evaluated by a standard Sawyer-Tower circuit at 100 Hz. The density of the sintered samples was measured using the Archimedes principle.

A Disco DAD 321 automatic dicing saw, equipped with a flange type diamond saw blade of 70 μm thickness and 55 mm outer diameter (Disco NBC-Z 2050 55×0.07×40), was used to carry out the dicing operation for fabricating the 1-3 BNKLBT-1.5/epoxy 1-3 DF composites. Two perpendicular sets of equal spaced grooves were cut into the BNKLBT-1.5 disks. Due to blade vibration, the resulting grooves in the disk were about 77–81 μm wide (~10%–15% wider than the blade thickness). Therefore, by making different number of cuts per direction (cpd), composite disks with different BNKLBT-1.5 element widths (L) and different volume fractions ϕ of BNKLBT-1.5 from 0.60–0.89 were obtained. Then filling of epoxy [Ciba Araldite epoxy (Resin LY5210+Hardener HY2954 in a weight ratio of 1:0.53)] under vacuum was carried out. The samples were placed in an oven under 40 °C for 14 h for complete curing.

For the 1-3 fiber/epoxy FP composites, sintered BNKLBT-1.5 ceramic fibers were aligned in a plastic tube with diameter of 6 mm and filled with epoxy. Ciba Araldite epoxy was used as the matrix material. The epoxy was carried under the same condition described above and a ceramic fiber/epoxy 1-3 composite rod was formed. Then the rod was sliced into composite disks and polished to a proper thickness.

All the composite disks were painted with an air-dried silver paint (G3691 Agar Scientific) as electrodes on both top and bottom surfaces of the disk. The composite was polarized at 25 °C under an electric field of 4.0 MV/m for 10 min in a silicone oil bath.

The d_{33} piezoelectric coefficient of the dc poled ceramic fibers were measured by a ZJ-3D d_{33} meter from Beijing Institute of Acoustics. The impedance and phase versus frequency spectra of the samples were measured using an impedance/gain phase analyzer (Hewlett Packard 4294). The analyzer was also used to measure the capacitance and dielectric loss of the samples.

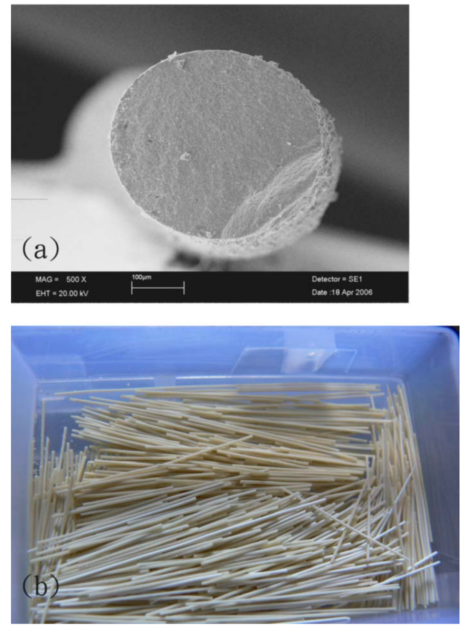

FIG. 1. (Color online) (a) SEM micrograph and (b) photograph of sintered BNKLBT-1.5 fibers.

RESULTS AND DISCUSION

The scanning electron microscopy (SEM) micrograph of the cross section of a sintered BNKLBT-1.5 fiber is shown in Fig. 1(a) and Fig. 1(b) shows the photograph of a sintered BNKLBT-1.5 fibers. The sintered fibers are straight, dense, and crack-free. It indicates that the fibers fabricated by powder extrusion method have good quality when both the pyrolysis and sintering processes are well controlled.

The polarization-electric field (*P-E*) loop measurement of BNKLBT fiber was performed using a Sawyer-Tower

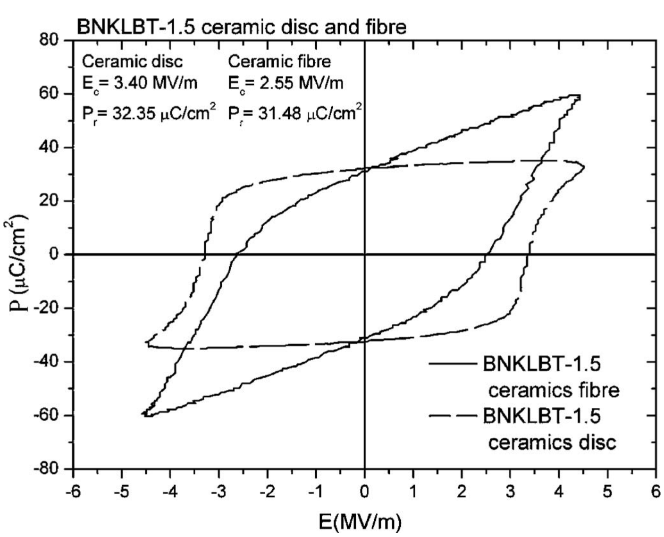

FIG. 2. *P-E* loops of BNKLBT fiber and disk.

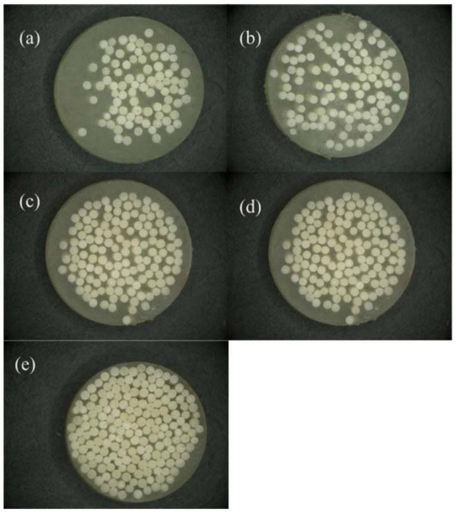

FIG. 3. (Color online) Photographs of 1-3 fiber/epoxy FP composites with different ceramics volume fractions (a) ϕ=0.26, (b) ϕ=0.3, (c) ϕ=0.4, (d) ϕ=0.54, and (e) ϕ=0.65, respectively.

bridge circuit. The *P*-*E* loops of the fiber are shown in Fig. 2. The remnant polarization (P_r) of the fiber is about 31.5 $\mu C/cm^2$, which is comparable with the bulk ceramic sample ($P_r \sim 32.4$ $\mu C/cm^2$). The coercive field (E_c) of the fiber ($E_c \sim 2.6$ kV/mm) is lower than that of the ceramics disk (E_c=3.4 kV/mm).

The properties of the 1-3 composites with different ceramic volume fractions (ϕ) and fabricated by different techniques are listed in Table I and the properties of pure ceramics disk, ceramics fiber, and pure epoxy are also listed. The properties of the ceramic fibers are comparable with ceramic disks showing that the fibers have good quality. Figures 3 and 4 show the photographs of the 1-3 FP composites and 1-3 DF composites with different ceramics volume fractions, respectively.

Performances of 1-3 piezocomposites can be predicted by the modified series and parallel models[16,17] as follows:

$$\bar{\rho} = \phi\rho + (1-\phi)\tilde{\rho}, \quad (1)$$

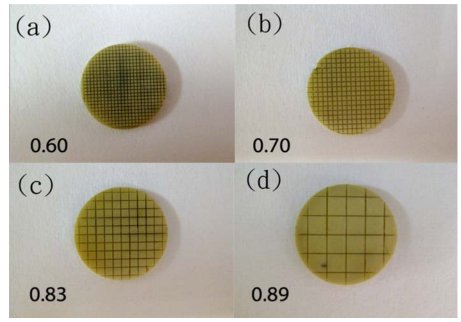

FIG. 4. (Color online) Photographs of 1-3 ceramic/epoxy DF composites with different ceramics volume fractions (a) ϕ=0.60, (b) ϕ=0.70, (c) ϕ=0.83, and (d) ϕ=0.89, respectively.

$$\bar{d}_{33} = \frac{\phi d_{33}\tilde{s}_{11}}{S(\phi)}, \quad (2)$$

$$\bar{\varepsilon}_{33}^{T} = \phi\varepsilon_{33}^{T} + (1-\phi)\tilde{\varepsilon}_{11} - \frac{\phi(1-\phi)d_{33}^{2}}{S(\phi)}, \quad (3)$$

$$S(\phi) = \phi\tilde{s}_{11} + (1-\phi)s_{33}^{E}, \quad (4)$$

$$\bar{k}_{33} = \frac{\bar{d}_{33}}{\sqrt{\bar{\varepsilon}_{33}^{T}\bar{s}_{33}^{E}}}, \quad (5)$$

$$\bar{g}_{33} = \frac{\bar{d}_{33}}{\bar{\varepsilon}_{33}^{T}}. \quad (6)$$

In these equations, the materials parameters of epoxy were denoted by a curved bar on top of the parameters. The effective materials parameters of the composite were denoted with a bar.

This model is based on the equal-strain assumption which can well predict the properties of 1-3 piezocomposites with high ceramic volume fractions. Some important properties are predicted and the results are presented in Fig. 5. The solid line represents the calculated results and the solid squares (for epoxy and BNKLBT-1.5), circles (for FP com-

TABLE I. The properties of BNKLBT fibers, bulk samples, pure epoxy, and 1–3 ceramic/epoxy 1–3 composites with different ceramics volume fractions.

Parameters	Epoxy	ϕ=0.26 (FP)	ϕ=0.3 (FP)	ϕ=0.4 (FP)	ϕ=0.54 (FP)	ϕ=0.65 (FP)	ϕ=0.60 (DF)	ϕ=0.70 (DF)	ϕ=0.83 (DF)	ϕ=0.89 (DF)	Ceramic disc	Ceramic fiber
Density (kg/m^3)	1133	2570.5	2525.3	2953.6	3633.4	3780.5	3890	4350	4943	5229	5800	5770
ε_{33} at 1 kHz	5.15	162.7	253.5	253.5	322	424.5	450.5	505.97	610.853	689.835	684.3	786.8
d_{33} (pC/N)	0	142	147	156	151	161	156	160	164	170	154.7	155.5
g_{33} ($\times 10^{-3}$ V m/N)	0	9.86	6.55	6.95	5.33	4.29	3.91	3.57	3.03	2.78	2.55	2.23
tan δ (%) at 1 kHz	1.4	3.9	4	4.2	4.9	3.9	3.2	3.1	3.5	3.6	1.67	3.52
k factor	0	0.56	0.557	0.5	0.5	0.53	0.50	0.53	0.52	0.364	k_t=0.519 k_p=0.309	k_{33}= 0.549
Acoustic impedance Z (MRayl)	2.99	8.62	8.72	11.31	13.72	15.89	13.71	17.81	20.67	25.13	26.41	26.41

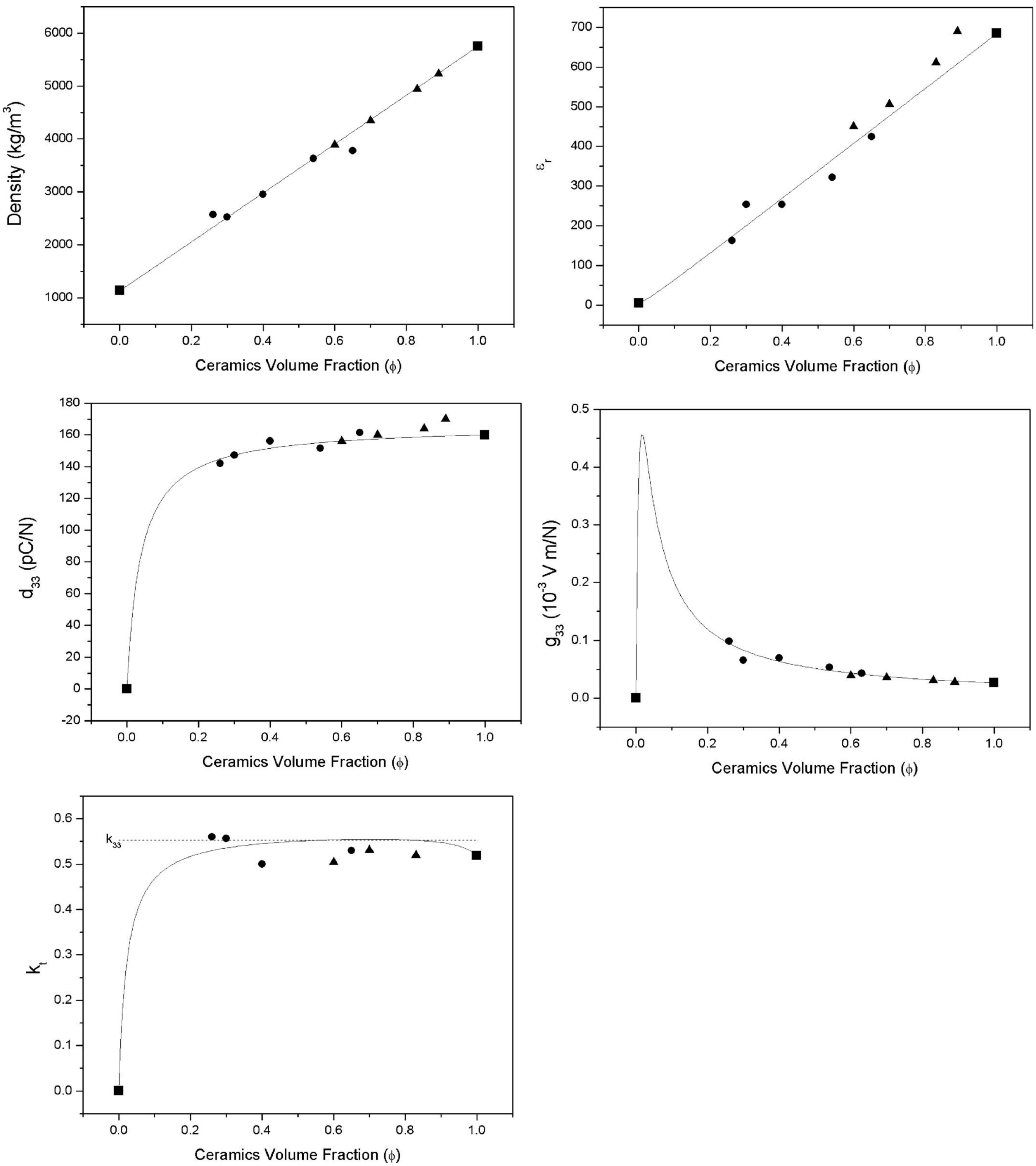

FIG. 5. The calculated and experimental results of 1-3 piezocomposites include density, relative permittivity ε_r, piezoelectric strain constant d_{33}, piezoelectric voltage constant g_{33}, and electromechanical coupling coefficient k_t (circle, FP composites; triangle, DF composites).

posites), and triangles (for DF composites) represent the experimental results. It shows that the results agree quite well with the theoretical model. The electromechanical coupling factor (k_t) of the 1-3 DF composites with volume fraction of $\phi=0.89$ cannot be determined accurately due to the mode coupling effect in the composites. For the $\phi=0.89$ composite, the pillar-shaped ceramic element inside the 1-3 composites with the length and width (L) of ~1.6 mm and thickness (t) of ~1 mm. Based on the mode coupling model,[16,17] L/t ratio is an important factor and coupling between the thickness and transverse resonance modes occurs when the L/t ratio is close to 1.5. For BNBT-6, the mode coupling occurs when $L/t=1.45$.[18,19] Figure 6 shows the frequency impedance/phase spectra of the 1-3 DF composites with ce-

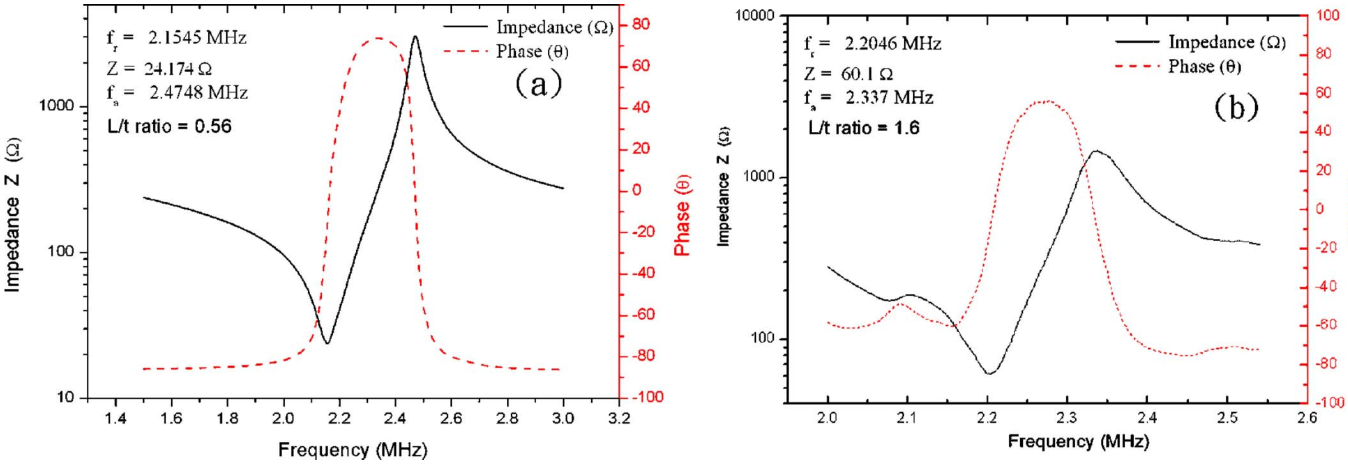

FIG. 6. (Color online) The frequency-impedance/phase spectrum of a 1-3 ceramic/epoxy composites disks with (a) $\phi=0.70$ and (b) $\phi=0.89$, respectively.

ramics volume fractions of 0.70 and 0.89, respectively. It is seen from Fig. 6(b) that the resonance peak split into two peaks in the $\phi=0.89$ composite.

The major advantage of 1-3 ceramic/epoxy composites is the flexibility in adjusting the properties of the composites by varying the ceramic volume fraction to fit specific device applications. Ultrasonic transducer for nondestructive evaluation (NDE) is one of the potential applications for the composites. Most of the NDE transducer uses aluminum as housing and front matching layer. The acoustic impedance matching between the front layer and the sensing element is important for efficient energy transfer. The acoustics impedance of aluminum is 17 MRayl, which is close to the composite with ceramic volume fractions of 0.65 (~15.89 MRayl) and 0.70 (~17.81 MRayl). The good acoustics impedance matching can improve the performance of the transducer.

CONCLUSION

BNKLBT-1.5 ceramic fibers have been prepared successfully using a powder-based extrusion method. The ceramic fibers were dense and crack-free. Measurements showed that the fibers have properties comparable with the bulk ceramic samples. Both ceramic fibers and bulk ceramic disks are used to fabricate 1-3 ceramic/epoxy composites with different ceramic volume fractions by using fiber pick-and-place (FP) and dice-and-fill (DF) techniques. The piezoelectric properties of the composites were measured and compared with the theoretical model and it was found that the experimental results agree quite well with the model. The lead-free ceramics fibers/epoxy 1-3 composites can enhance the electromechanical coupling coefficient and provide a good acoustics impedance matching with aluminum which is useful for ultrasonic transducer applications.

ACKNOWLEDGMENTS

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