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Lead-free piezoelectric BNKLT 1–3 composites

K. H. Lam · M. S. Guo · D. M. Lin ·
K. W. Kwok · H. L. W. Chan

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Abstract $Bi_{0.5}(Na_{0.725}K_{0.175}Li_{0.1})_{0.5}TiO_3$ (abbreviated as BNKLT) is a soft-type piezoelectric ceramics with good piezoelectric properties and strong ferroelectricity at room temperature. The composites with different volume fractions of BNKLT ranging from 0.59 to 0.86 were fabricated by the dice-and-fill method. The composites have been characterized by the resonance techniques and it was found that the composites have good piezoelectric properties that agreed quite well with theoretical modeling. Those composites have potential to be transducer elements in various applications.

Introduction

Piezoelectric composites have been studied to obtain properties superior to a single phase material [1–3]. There are ten connectivity patterns according to the connectivity of the active element and passive matrix phase [3]. Connectivity is defined as the number of dimensions in which a phase is self-connected while 1–3 is one of the ten connectivities in biphasic composites. The idea of 1–3 composites has been developed for a wide range of applications in recent years [4–9]. Among various types of 1–3 composites, piezoelectric 1–3 ceramic/polymer composites consist of piezoelectric rods embedded in a polymer phase have been widely used in transducer applications [10–13]. Those composites combine the advantages of the ceramics and polymer phases. The 1–3 connectivity enhances the electromechanical coupling in the thickness mode effectively. Besides, it maintains the high piezoelectric characteristics of ceramics and provides low acoustic impedance because of the incorporation of the passive phase. The characteristics of 1–3 composites can be adjusted by tailoring the ceramic volume fraction to meet the specific requirements of various applications. In the past, many models have been introduced for investigating the physical and electrical properties of 1–3 composites [14, 15]. A large electromechanical coupling coefficient k_t can be obtained that approached the longitudinal coupling factor k_{33} of the ceramic rods in the composites.

The most widely used piezoelectric ceramics are lead-based ceramics, especially $Pb(Zr,Ti)O_3$ (PZT), because of their superior piezoelectric properties [16]. Recently, with concern to the environmental pollution of PbO evaporation, it is desired to use lead-free materials for environmental protection. Lead-free piezoelectric ceramics have widely attracted considerable interest to replace the lead-based material systems [17]. $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) is considered to be one of the good candidates of lead-free piezoelectric ceramics because of its large remanent polarization [18]. However, due to their high coercive field, pure BNT ceramics are difficult to pole to possess much lower piezoelectric properties compared with PZT ceramics. In order to improve the properties of BNT ceramics, new $[Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}]TiO_3$ lead-free piezoelectric ceramics (BNKLT − x/y) were proposed [19, 20]. The partial substitution of Na^+ by K^+ and Li^+ effectively decreases the coercive field of the ceramics. Simultaneously, the strong ferroelectricity is still maintained with good piezoelectric properties [21].

K. H. Lam (✉) · M. S. Guo · D. M. Lin ·
K. W. Kwok · H. L. W. Chan
Department of Applied Physics and Materials Research Centre,
The Hong Kong Polytechnic University, Hunghom, Hong Kong,
China
e-mail: kokokh.lam@polyu.edu.hk

In this study, BNKLT ceramics with good piezoelectric performance was used as an active element of piezoelectric ceramic/epoxy 1–3 composites. The composites were characterized by the resonance techniques and compared with the theoretical modified series and parallel modeling.

Experimental

BNKLT ceramics was prepared by a conventional ceramic technique. Industrial-grade metal oxides or carbonates powders were used as starting raw materials. The oxides and carbonates with a stoichiometric ratio were mixed and then calcined at 850 °C for 2 h. BNKLT ceramic discs of 12.7 mm diameter were fabricated by dry pressing and sintering at 1,100–1,200 °C for 2 h. Before poling, co-fired silver paste was applied to the two flat surfaces of the discs as electrodes. They were poled in silicone oil along their thickness direction by applying a D.C. field of 5 kV/mm at 100 °C for 20 min. After poling, the ceramic discs were short-circuit to remove the injected charges.

BNKLT/epoxy 1–3 composites were fabricated using a dice-and-fill technique. Poled ceramic disc was cut in one direction using an automatic dicing saw (Disco DAD 321) with a blade of 70 μm thickness. The aspect ratio (thickness to width ratio) of the BNKLT rods inside the composites was higher than two to avoid mode coupling. Araldite LY 564/Aradur 2954, a passive phase of the composites due to its low-viscosity and soft characteristics, was used to fill the grooves in the diced disc. The epoxy in the sample was degassed in vacuum for 30 min. After the epoxy was cured at 80 °C for 1 h and 140 °C for 8 h, a second set of cuts perpendicular to the first direction was made. After filling the second set of cuts with epoxy, the composite was dried under the same condition mentioned above. Excess epoxy and ceramics left at the bottom were polished away with silicon carbide abrasive papers. After polishing, the composites were electroded with air dried silver paint for electrical characterization.

Density, ρ, of the samples was measured based on the Archimedes' principle using an electronic balance. The piezoelectric strain coefficient, d_{33}, was measured by a d_{33} meter (ZJ-3B) which is supplied by the Beijing Institute of Acoustics, Academia Sinica. The impedance and phase of the samples were measured using an impedance/gain phase analyzer (Agilent 4294A). Electromechanical coupling coefficient in the thickness direction k_t and acoustic impedance Z_a were determined following the IEEE standard on piezoelectricity [22] by measuring the resonant frequency, f_r and anti-resonant frequency, f_a of the thickness mode resonance in the samples. To model the performance of the 1–3 composites, materials parameters of the passive matrix were characterized. The acoustic velocity and the elastic properties of a cured epoxy were determined using the ultrasonic immersion method [23].

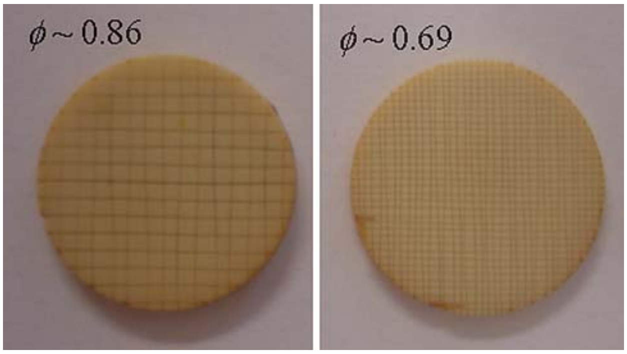

Fig. 1 Photographs of BNKBT/epoxy 1–3 composites with different ϕ

Results and discussion

As shown in Fig. 1, BNKLT ceramic/epoxy 1–3 composites with ceramic volume fractions ϕ of 0.59–0.86 have been fabricated. The measured electrical impedance and phase versus frequency spectra of (a) a BNKLT/epoxy 1–3 composite and (b) a BNKLT ceramic disc are shown in Fig. 2. Compared to the ceramics, the harmonics of a low-frequency resonance of the composite have been weakened. Due to the weak harmonics, a very pure thickness resonance can be observed without a significant mode coupling.

With the modified series and parallel model [2, 14], the theoretical performance of the composites can be calculated as a function of ϕ. The theoretical density ρ, piezoelectric coefficient d_{33}, electromechanical coupling coefficient k_t, piezoelectric voltage coefficient g_{33}, and acoustic impedance Z_a of the composites are determined by the following equations:

$$\rho = \phi\rho_{\mathrm{BNKLT}} + (1-\phi)\rho_{\mathrm{epoxy}} \tag{1}$$

$$d_{33} = \frac{\phi d_{33,\mathrm{BNKLT}} S_{11,\mathrm{epoxy}}}{\phi S_{11,\mathrm{epoxy}} + (1-\phi) S^{\mathrm{E}}_{33,\mathrm{BNKLT}}} \tag{2}$$

$$K_t = \sqrt{1 - \frac{C^{\mathrm{E}}_{33}}{C^{\mathrm{D}}_{33}}} \tag{3}$$

$$g_{33} = \frac{d_{33}}{\varepsilon^{\mathrm{T}}_{33}} \tag{4}$$

$$Z_a = \sqrt{\rho \cdot C^{\mathrm{D}}_{33}} \tag{5}$$

where s the elastic compliance, c the elastic stiffness, $\varepsilon^{\mathrm{T}}_{33}$ the relative permittivity of the samples, and ε_0 is the permittivity in free space ($\sim 8.85 \times 10^{-12}$ F/m).

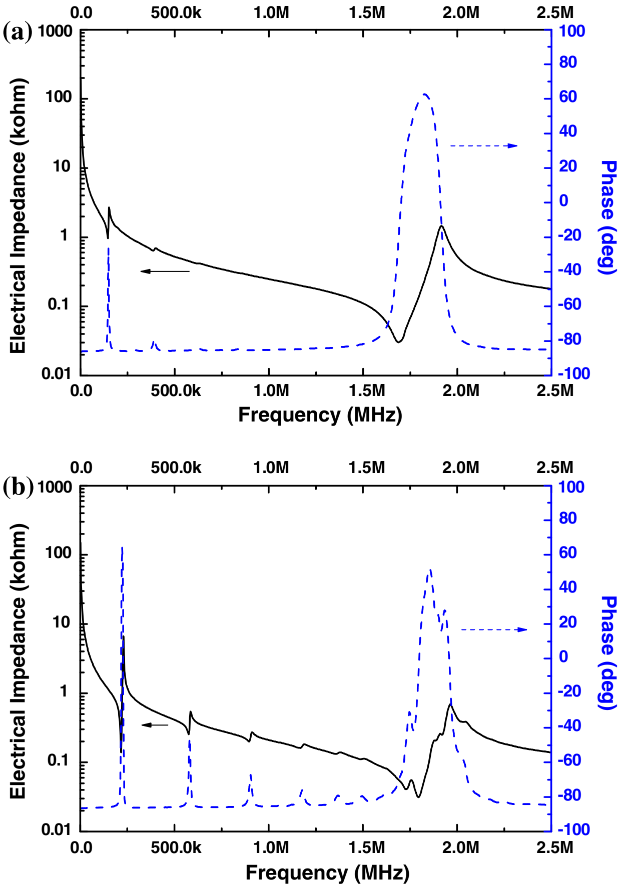

Fig. 2 Electrical impedance and phase versus frequency spectra for (**a**) a BNKLT/epoxy 1–3 composite with $\phi = 0.86$ and (**b**) a BNKLT bulk disc

The modified series and parallel model show that the piezoelectric parameters of the composites increase with ϕ due to the increase contribution of the active ceramic phase. As shown in Figs. 3 and 4, the density ρ and piezoelectric coefficient d_{33} of the composites increase monotonically as a function of ϕ. Although the experimental d_{33} of the composites is slightly lower than the theoretical values, the values are reasonable and the trend is similar to that in prediction. As expected, k_t can be enhanced effectively using the 1–3 connectivity as shown in Fig. 5. The k_t values of the BNKLT composites with different ϕ can also approach 0.56 which is higher than that of a BNKLT ceramic disc ($k_t \sim 0.44$) and comparable to its k_{33} value ($k_{33} \sim 0.58$). Compared to PZTs, the lead-free ceramics have low relative permittivity (~1,200 for BNKLT) so that the g_{33} value of lead-free ceramics is usually high. Since d_{33} of the composites can be maintained and ε_{33}^{T} of the composites increases with ϕ, g_{33} of the composites increase with the decrease contribution of the ceramic phase as shown in Fig. 6. It is one of the important parameters for sensor and transducer materials.

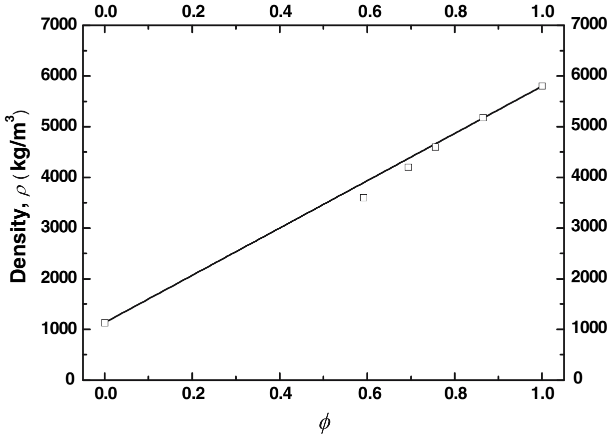

Fig. 3 Density ρ of the BNKLT/epoxy 1–3 composites as a function of ϕ. (Symbols: experimental data; Line: theoretical prediction)

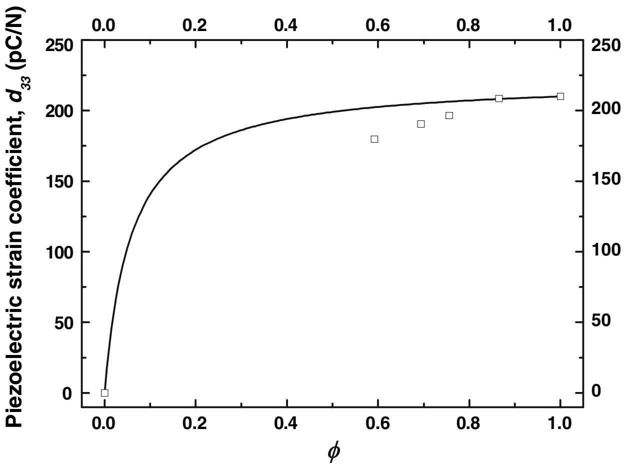

Fig. 4 Piezoelectric strain coefficient d_{33} of the BNKLT/epoxy 1–3 composites as a function of ϕ. (Symbols: experimental data; Line: theoretical prediction)

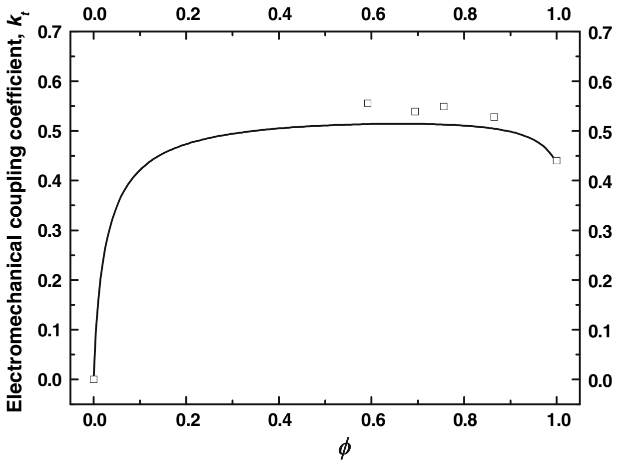

Fig. 5 Electromechanical coupling coefficient k_t of the BNKLT/epoxy 1–3 composites as a function of ϕ. (Symbols: experimental data; Line: theoretical prediction)

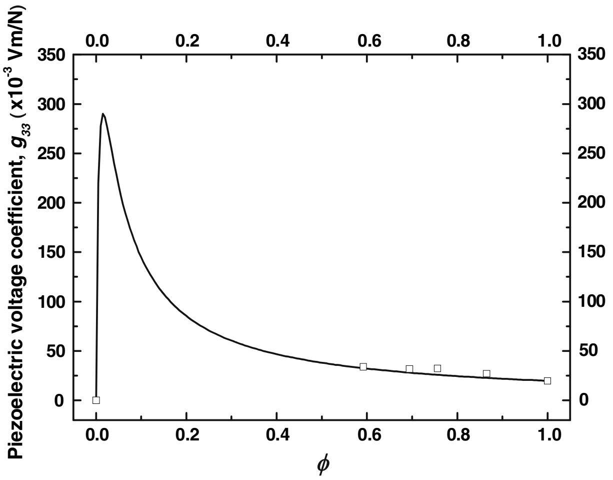

Fig. 6 Piezoelectric voltage coefficient g_{33} of the BNKLT/epoxy 1–3 composites as a function of ϕ. (Symbols: experimental data; Line: theoretical prediction)

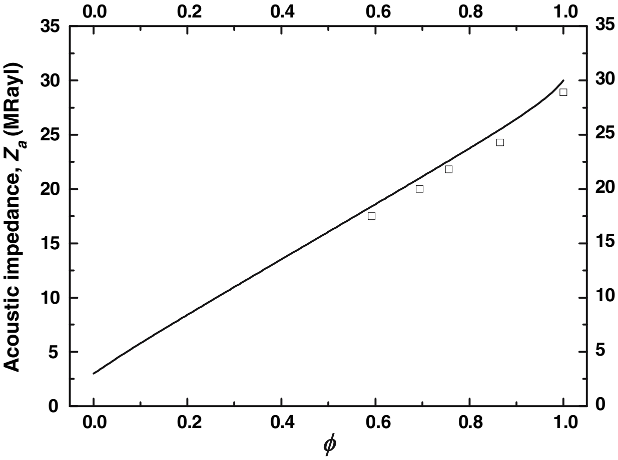

Fig. 7 Acoustic impedance Z_a of the BNKLT/epoxy 1–3 composites as a function of ϕ. (Symbols: experimental data; Line: theoretical prediction)

Figure 7 shows that Z_a of the composites increase almost linearly with ϕ. The experimental data is shown to have a good agreement with the modified series and parallel model.

Conclusion

The lead-free BNKLT/epoxy 1–3 composites with various BNKLT volume fractions have been fabricated using the dice-and-fill technique. The performance of the lead-free composites was characterized using the resonance technique. The composites have high k_t value of 0.55 which is comparable to the k_{33} value of a free ceramic rod. The experimental data agreed quite well with the prediction of the modified series and parallel model. With reasonable piezoelectric and electromechanical performance, the lead-free BNKLT composites have the potential to replace lead-based ones as the next generation of transducer materials.

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