Lead-free ceramics for pyroelectric applications

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(Received 27 November 2007; accepted 16 March 2008; published online 23 May 2008)

The use of lead-free materials has recently become a very important issue in environmental protection of the earth. Two groups of lead-free ceramics, $(K_{0.5},Na_{0.5})NbO_3$ based (KNN) and $Bi_{1-y}(Na_xK_{1-x})_yTiO_3$ based (BNKT), were studied for their thermal, dielectric, and pyroelectric properties as candidates for pyroelectric sensor applications. The BNKT-based ceramic, $[Bi_{0.5}(Na_{0.94}K_{0.05}Li_{0.016})_{0.5}]_{0.95}Ba_{0.05}TiO_3$ (BNKLBT), shows excellent pyroelectric properties when compared with KNN-based ceramic and lead zirconate titanate. Its properties were measured as follows: pyroelectric coefficient $p=360$ μC/m^2 K, pyroelectric figure of merit of current, voltage, and detectivity $F_i=221$ pm/V, $F_v=0.030$ m^2/C, and $F_d=14.8$ μPa$^{-1/2}$. With these outstanding pyroelectric properties, the BNKLBT ceramic can be a promising material for pyroelectric sensor applications. The BNKLBT ceramic with different thicknesses (i.e., 0.3, 0.5, and 0.7 mm) have been used as the sensing element for fabricating infrared detectors. The current responsivity of the sensors was evaluated as functions of frequency.
[DOI: 10.1063/1.2927252]

I. INTRODUCTION

Ferroelectric ceramics such as lead titanate (PT) and lead zirconate titanate (PZT) are widely used in sensor, actuator, and transducer applications due to their superior piezoelectric and pyroelectric properties. However, the use of lead-based ceramics has caused serious environmental pollution. The toxicity of these materials either during the manufacturing process (evaporation of lead) or after making the device is of serious concerns. Therefore, there is a great need to develop lead-free ceramics for replacing the lead-containing ceramics in various applications.

Bismuth sodium titanate, $Bi_{0.5}Na_{0.5}TiO_3$ (BNT), is a perovskite ferroelectric discovered in 1960 by Smolenskii *et al.*[1] BNT shows good ferroelectric properties ($P_r=38$ μC/cm^2) and has a high Curie temperature ($T_C=320$ °C). However, the poling effectiveness of this material is fair due to its high leakage current. A number of BNT-based lead-free ceramics, such as $Bi_{0.5}Na_{0.5}TiO_3-BaTiO_3$ (BNT-BT),[2] $Bi_{0.5}Na_{0.5}TiO_3-Bi_{0.5}K_{0.5}TiO_3$ (BNKT),[3] and $Bi_{0.5}Na_{0.5}TiO_3-NaNbO_3$ (BNT-NN),[4] have been developed with a view to improve their performance. Nagata *et al.*[5] first reported that the piezoelectric properties of some compositions in the multicomponent system $Bi_{0.5}Na_{0.5}TiO_3-Bi_{0.5}K_{0.5}TiO_3-BaTiO_3$ (BNKT-BT) showed significant improvement. Wang *et al.*[6,7] studied the system in detail including dielectric, piezoelectric, and ferroelectric properties and also the depolarization temperature. Besides, another lead-free system $K_{0.5}Na_{0.5}NbO_3$ (KNN), consisted of the solid solution of ferroelectric $KNbO_3$ and antiferroelectric $NaNbO_3$, also displays good ferroelectric properties ($P_r=33$ μC/cm^2) and large electromechanical coupling factors. By incorporating with different end members, such as $LiNbO_3$ and $SrTiO_3$, the materials show good sinterability and piezoelectric properties.[8–10] Lang *et al.*[11] reported the piezoelectric and pyroelectric properties of the KNN-based ceramic. The d_{33} and p coefficient were found to be 289 pC/N and 160 μC/m^2 K, respectively.

The main objective of this work is to study the pyroelectric properties of KNN-based and BNKT-based lead-free ceramics as well as to select a suitable sample to fabricate an infrared sensor. The preparation process of the lead-free ceramic samples was described. The dielectric, thermal, and pyroelectric properties of all samples were evaluated. Infrared sensors based on the selected lead-free ceramic samples were constructed and their performance was measured as a function of frequency.

II. SAMPLE PREPARATION

The lead-free ceramics, KNN and BNKT based, were prepared by conventional ceramic fabrication technique. Reagent grade metal oxides or carbonates powder were used as starting raw materials. Four different systems of ceramic powder were fabricated and the chemical formulas are listed below:

(a) $[(K_{0.5}Na_{0.5})_{0.96}Li_{0.04}](Nb_{0.8}Ta_{0.2})O_3$ (KNLNT);
(b) $[(K_{0.5}Na_{0.5})_{0.96}Li_{0.04}](Nb_{0.84}Ta_{0.1}Sb_{0.06})O_3$ (KNLNTS);
(c) $[Bi_{0.5}(Na_{0.95}K_{0.05})_{0.5}]_{0.95}Ba_{0.05}TiO_3$ (BNKBT);
(d) $[Bi_{0.5}(Na_{0.94}K_{0.05}Li_{0.016})_{0.5}]_{0.95}Ba_{0.05}TiO_3$ (BNKLBT).

The raw materials were mixed together by ball milling using zirconia balls in ethanol, and then dried and calcinated at about 800–900 °C for 2–4 h. After calcination, the mixture was ball milled again and mixed thoroughly with a polyvinyl alcohol (PVA) binder solution and then pressed into disk samples. The samples were finally sintered at 1100–1200 °C for 2–3 h in air. The ceramic discs were polished with ul-

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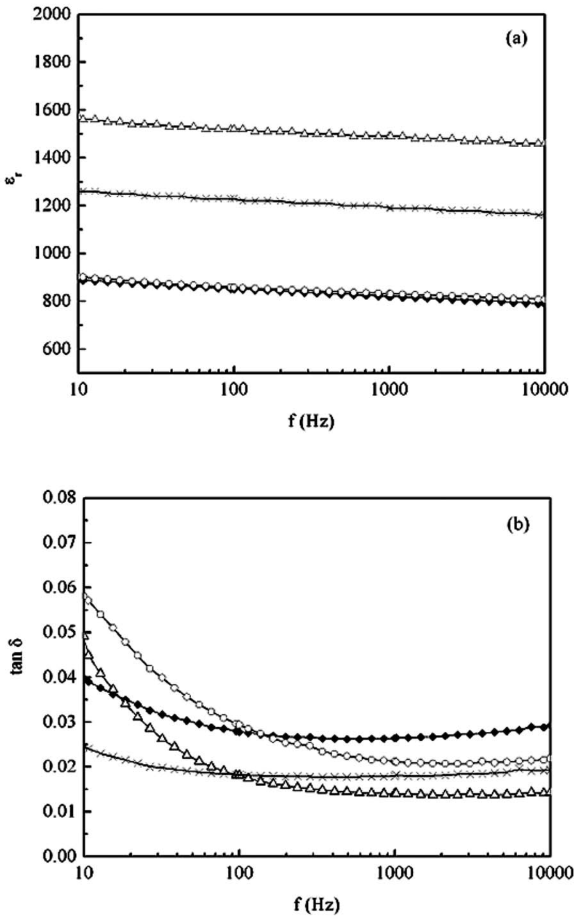

FIG. 1. Frequency dependence of (a) ε_r and (b) tan δ for the lead-free ceramics at room temperature: ×—KNLNT; △—KNLNTS; ♦—BNKBT; ○—BNKLBT.

trafine wet silicon carbide abrasive papers before electroding. The resulting discs were 10 mm in diameter and ~0.9 mm thick. Silver paste was coated on both sides of sintered ceramic samples and fired at 810 °C to form electrodes. A dc poling process was applied to induce the pyroelectric property of the samples. For KNN-based ceramics, the samples were poled by a dc field of 5 MV/m for 30 min at 180 °C. For BNKT-based ceramics, the samples were poled by a dc field of 4 MV/m for 10 min at room temperature. All poled samples were put into an oven and kept at 60 °C for at least 10 h under short-circuit condition to remove any unwanted trapped charges.

III. PROPERTIES OF LEAD-FREE CERAMICS

The dielectric properties of the samples were measured as a function of frequency at room temperature using a broadband dielectric spectrometer (Novocontrol Technologies GmbH & Co. KG, Germany). To separate the real pyroelectric response from the thermally stimulated discharge in the materials, an ac method[12] was used to determine the pyroelectric coefficient of the samples. The specific heat of the samples was measured using a Perkin Elmer DSC7 differential scanning calorimeter, and the density was measured by weighing the disc in air and in water and then applying the Archimedes principle.

Figure 1 shows the frequency dependence of the relative permittivity (ε_r) and dielectric dissipation factor (tan δ) for the lead-free ceramics. It can be seen that both ε_r and tan δ decrease with increasing frequency. At relatively low frequency ($f<100$ Hz), tan δ depends strongly on frequency. This is a common feature observed in ferroelectric materials concerned with ionic conductivity.[13] As the frequency increases, the effect of ionic conductivity becomes small, and the tanδ shows weak frequency dependence.

The pyroelectric coefficient p and the specific heat c_p of the lead-free ceramic samples were measured at room temperature. Besides, the figures of merit[14] (FOM) related to the performance of the materials used as the pyroelectric sensing elements have been calculated. The current FOM F_i is given by

$$F_i = \frac{p}{c_v}, \tag{1}$$

where $c_v = \rho c_p$ is the volume specific heat, and ρ the density of the sample. The voltage FOM F_v is given by

$$F_v = \frac{p}{c_v \varepsilon_r \varepsilon_o}, \tag{2}$$

where ε_o is the permittivity of free space ($=8.854\times10^{-12}$ F/m). The detectivity FOM F_v is given by

$$F_D = \frac{p}{c_v \sqrt{\varepsilon_r \varepsilon_o \tan\delta}}. \tag{3}$$

Table I shows the pyroelectric coefficient and figures of merit of the lead-free ceramic samples. For comparison, the pyroelectric properties of the PZT are also given in Table I. The p values of BNKT-based lead-free ceramics are higher than that of KNN-based ceramics. For the BNKBT sample doped with 1.6 mol % of Li (BNKLBT), the p value is increased ($=360$ μC/m^2 K), which is nearly 87% to that observed in PZT sample. With its low c_v and ε_r, BNKLBT shows superior value of FOMs compared with other lead-free ceramics and PZT. Hence, it can be a suitable candidate

TABLE I. Pyroelectric coefficient and figures of merit of the PZT and lead-free ceramic samples.

Sample	ε_r (at 100 Hz)	tan δ (at 100 Hz)	ρ (kg/m^3)	c_v ($\times10^6$ J/m^3 K)	p (μC/m^2 K)	F_i ($\times10^{-12}$ m/V)	F_v (m^2/C)	F_D (μPa$^{1/2}$)
KNLNT	1230	0.0182	5081	0.263	165	123.5	0.011	8.82
KNLNTS	1520	0.0181	4556	0.448	190	93.1	0.007	5.98
BNKBT	853	0.0278	5800	0.288	325	194.6	0.026	13.43
BNKLBT	858	0.0294	5770	0.283	360	220.5	0.029	14.75
PZT	1990	0.0140	7700	0.380[a]	414[a]	141.5	0.008	9.01

[a]The figures of merit are calculated from c_v and p values taken from Lam *et al.* (Ref. 16).

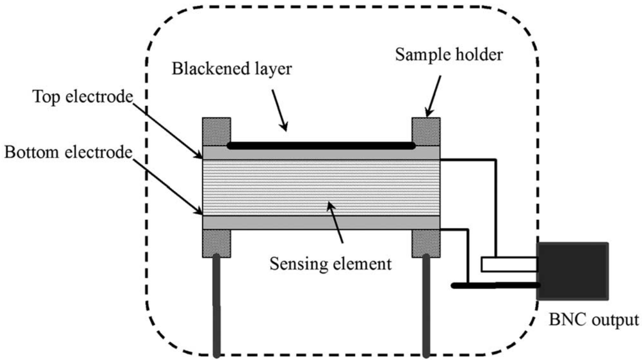

FIG. 2. Schematic diagram of the pyroelectric sensor.

to replace the lead-based ceramics to be fabricated for a pyroelectric sensor.

IV. SENSOR FABRICATION

The BNKLBT lead-free ceramic samples were used as the sensing materials for the pyroelectric sensors. Sensing elements of different thicknesses (i.e., 0.3, 0.5, and 0.7 mm) were prepared. A chromium-gold (Cr/Au) electrode of diameter 8 mm was sputtered on both surfaces of the samples. To enable a high absorption in the spectral region of interest, the surface of the element to be irradiated was coated with a thin graphite layer. The element was then mounted in a holder and put in the shielding box, as shown in Fig. 2.

V. SENSOR PERFORMANCE

The current responsivity of the pyroelectric sensors with lead-free BNKLBT ceramic as the sensing element was measured in the range of 60–600 Hz using the experimental setup shown in Fig. 3. An infrared laser (Lepton IV, $\lambda = 690$ nm) with power controller (LDC 400) produces a time dependent laser intensity. The diameter of the laser beam is 6 mm. A lock-in amplifier (SR 830) was used to provide a sinusoidal modulation to the laser diode controller. Thus, the laser diode produced a modulated radiation on the sensor and then a pyroelectric current was generated. The current was first amplified by a low-noise current preamplifier (SR 570) and then was transmitted to the lock-in amplifier. The pyroelectric current I was measured by the lock-in amplifier. The incident power W of the laser was measured by the Newport optical power meter (Model 835), and 90% absorption by the graphite layer was assumed.[15] The current responsivity R_i can be calculated by

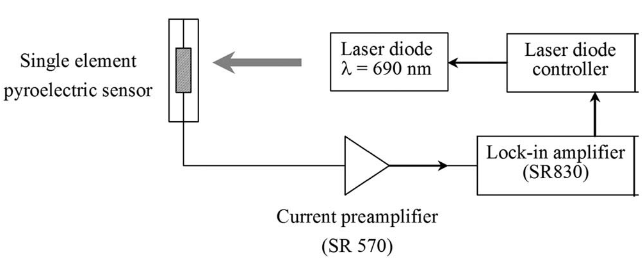

FIG. 3. Schematic setup of the measurement of current response to incident radiation.

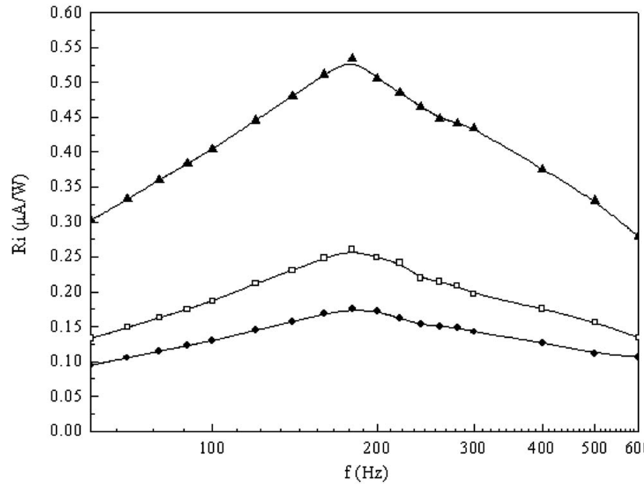

FIG. 4. Frequency dependence of R_i for lead-free BNKLBT pyroelectric sensors. Element thickness: ●—0.7 mm; □—0.5 mm; ▲—0.3 mm.

$$R_i = \frac{I_{\rm rms}}{W_{\rm rms}}. \tag{4}$$

The current responsivities R_i of the lead-free BNKLBT pyroelectric sensors as a function of frequency are shown in Fig. 4. In real sensor, heat loss to the surroundings increase when the thermal diffusion length L tends to be larger than the thickness of the sensing element, and weak responsivity R_i is observed at low frequencies. Since L is inversely proportional to the frequency f, R_i then increases with the frequency and reaches a maximum value at $f = 180$ Hz. However, as the frequency further increases, L becomes smaller than the thickness of the sensing element, the thermal wave does not fully penetrate the element. The amount of thermal energy stored in the thermal capacity of the graphite layer and top electrode increases, leading to decrease in R_i at high frequencies. On the other hand, by thinning the sensing element, R_i is enhanced significantly.

VI. CONCLUSION

The dielectric, thermal, and pyroelectric properties of KNN-based and BNKT-based lead-free ceramics have been studied. Among the samples, the $[Bi_{0.5}(Na_{0.94}K_{0.05}Li_{0.016})_{0.5}]_{0.95}Ba_{0.05}TiO_3$ (BNKLBT) shows excellent pyroelectric properties, and has better pyroelectric figure of merit than PZT. The BNKLBT ceramics have been used to fabricate into pyroelectric sensors. The current responsivity increases with the frequency and reach to the maximum at 180 Hz. At higher frequency, the current responsivity decreases because the heat transfer from the graphite absorber and top electrode become less efficient. By reducing the element thickness, the current responsivity increases significantly.

ACKNOWLEDGMENTS

This work was supported by the Hong Kong Polytechnic University grants (Project Nos. 1-BB95 and 1-BBZ3) and the Centre for Smart Materials of the Hong Kong Polytechnic University.

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