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PZT-type materials with improved radial piezoelectric properties

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Abstract

The goal of this work is to prepare doped PZT-type materials with improved radial piezoelectric properties. Ceramic materials were obtained by solid-state reaction at different sintering temperatures. SAED, bright field TEM and HRTEM methods were used for the microstructure studies. The influence of the composition and nanostructure on the dielectric and piezoelectric properties of the materials is discussed. One of the materials with high coupling constant was used in the construction of a miniature flexural ventilator. Designated to function at an emf of 220 V/50 Hz, this device is characterized by high efficiency, reliability and low energy consumption.

Keywords: PZT; Electron microscopy; Dielectric properties; Piezoelectric properties; Functional applications

1. Introduction

The chemical composition, the manufacturing route, the type of the electrodes and poling conditions are determining the properties of the PZT-type materials.[1] For each application, specific physical properties as well as various vibration modes associated with the shape of the piezoelectric elements are necessary.[2]

The purpose of this study is to fabricate by conventional process a PZT material both with donor and acceptor additives, to investigate the effect of the PbO excess and repoling processes on the electro-mechanical properties of the piezoelectric elements. The existence of domains and domain walls is evidenced in the samples sintered at 1280 °C, by TEM method. A bimorph was used to the construction of a miniature ventilator.

2. Experimental

Starting from a reference material with the composition in the morphotropic tetragonal–rhombohedral phase boundary, namely $PbTi_{0.48}Zr_{0.52}O_3$,[1] two type of substitution were made: a higher valence ion Bi^{3+} and Nb^{5+} for Pb^{2+} and Ti^{4+}, respectively, and a lower valence ion (Li^{+}) for Zr^{4+}. It is expected that these substitutions enhance the piezoelectric properties. A reacted and ground material with the composition $Pb_{0.992}Bi_{0.008}\,(Ti_{0.463}Nb_{0.02}Zr_{0.51}Li_{0.007})\,O_3$, denoted PZT-BNL, was produced by a solid-state reaction technique. High purity raw materials, PbO, ZrO_2, TiO_2, Bi_2O_3, Nb_2O_5, and Li_2CO_3 (>99%), were used. An excess of PbO is added to the above composition, with the PbO content varying from 1% to 4%. Disks of about 17 mm in diameter pressed uniaxially, without binder, were embedded in a PZT powder with the same composition and sintered in a range of temperature between 1200 °C and 1300 °C. The disks with nickel electrodes,[3] chemically deposited, were poled in silicone oil bath at 220 °C, under of an electric field of 3 kV/mm. Samples investigation was performed using a Philips CM 120 ST microscope operating at 100 kV and maximum magnification 1 050 000×. Samples were dispersed on ethylic alcohol and collected on 300 mesh formvar coated grids. HRTEM and SAED techniques were used for the morphological characterization and the checking of crystallographic phases on nano-areas, respectively.

The piezoelectric properties, carried out after 24 h after poling, were determined from the measurements of

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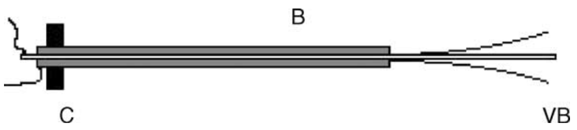

Fig. 1. Sketch of the flexural ventilator: C, clamping masses; B, piezoceramic bimorph; VB, vibrating blade.

capacitance, resonance and antiresonance frequency for radial modes, by using a Hewlet Packard 4149A Impedance/Gain–Phase Analyser. Samples made from the material PZT-BNL were subjected to five poling to improve some of the physical properties.[4]

The material PZT-BNL was used for the construction of the flexural ventilator. Two rectangular pieces of ceramic are fixed together with a metallic blade using a conductive resin (Fig. 1), their electrical polarization, being parallel. Electrical connections are made to both of the plates and to the central metallic blade, so that the system is connected in derivation. The system is clamped at one end at an "infinite mass".

The frequency response of the transducer (Fig. 2) was measured using a driving electrical oscillator with a peak-to-peak amplitude of the signal of 90 V. The amplitude at the end of the metallic blade was measured using an optical method. The mechanical response of the transducer versus the driving emf was measured in the same conditions as the previous measurement, and the obtained data are presented in Fig. 3.

The connection between the length of the ceramic bimorph and the resonance frequency was measured in very similar conditions but varying the position of the clamping point (Fig. 4).

3. Results and discussion

The results included in the Table 1 show that the material containing Bi, Nb and Li as additives, presents higher dielectric and piezoelectric properties compared with the undoped PZT material.[1] The addition of PbO in excess to the stoichiometric composition has an unfavorable influence on the dielectric and piezoelectric properties of the materials. The material PZT-BNL re-poled five times shows the highest values of the relative dielectric constant measured at 1 kHz, ε_r, and planar coupling coefficient k_P. These values are comparable with those of material PZT5A[5] used as a receiver or generator element in hydrophones, accelerometers, and vibration sensors. It seems that the domains are better oriented after a number of poling, enhancing the dielectric and piezoelectric constants.

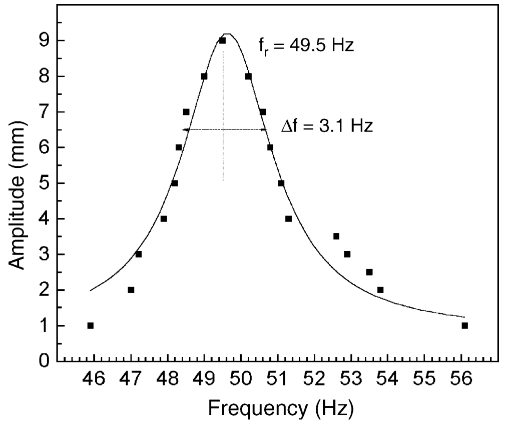

Fig. 2. The frequency response of the transducer; the driving emf is 90 V_{pp}.

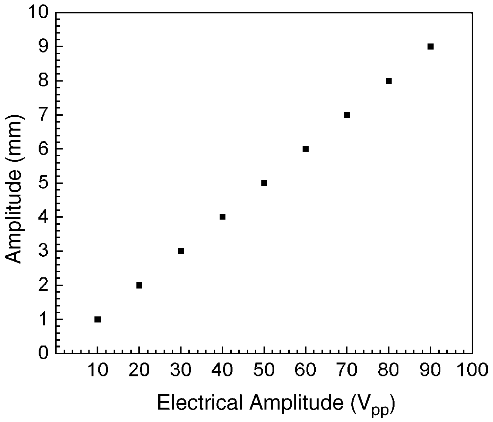

Fig. 3. The mechanical response of the ventilator vs. a variable driving emf.

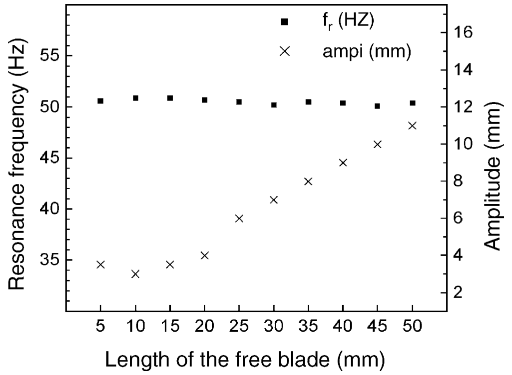

Fig. 4. The influence of the bimorph on the resonance of the ventilator.

Table 1
Physical properties of the PZT-type materials

PZT-type material	ε_r	k_P	k_{31}	Q_m	N_p^E
PZT-BNL	1324	0.557	0.28	67	2060
PZT-BNL + 1% PbO	1143	0.507	0.26	96	2150
PZT-BNL + 2% PbO	1259	0.545	0.28	89	2118
PZT-BNL + 3% PbO	985	0.462	0.24	106	2268
PZT-BNL + 4% PbO	1052	0.474	0.25	102	2219
PZT-BNL-Repoled 5 times	1635	0.58	0.32	76	1947
PZT 52/48 (undoped)[1]	1180	0.52	0.31	–	–
PZT5A[5]	1700	0.6	0.34	75	1980

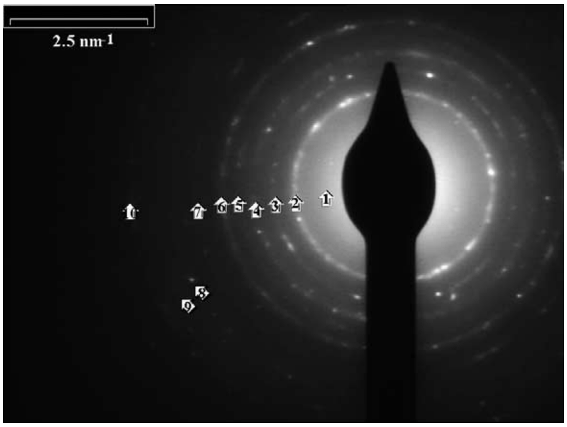

Fig. 5. SAED image of a sample made from PZT-BNL material, sintered at 1280 °C.

Table 2
Microstructural results on the PZT-BNL material for the lines 1–10 in Fig. 5

Line	d_{hkl} (nm)	hkl
1	0.403	(1 0 0)
2	0.278	(1 0 1)
3	0.226	(1 1 1)
4	0.196	(2 0 0)
5	0.174	(2 1 0)
6	0.161	(2 1 1)
7	0.141	(2 2 0)
8	0.124	(1 1 3)
9	0.114	(2 0 3)
10	0.105	(0 0 4)

3.1. *Microstructure consideration*

A shift of the morphotropic phase boundary is observed by doping the PZT (52/42) with Bi^{3+}, Nb^{5+}, Li^{+} ions. In the PZT-BNL materials only the tetragonal phase is present ($P4/mm$: $a = 0.403$ nm and $c = 0.414$ nm), as one can see from Fig. 5 and Table 2. The evidence of the nano-domains in the PZT-BNL materials is presented in Figs. 6–9. The selected area on the picture (Fig. 6) was filtered using a blob type filter and the result is shown on the right-down side of the image. The insert in Fig. 8 shows the FFT space of image with identified plans. (*) Plane (1 0 1) is forbidden for this crystal orientation [0 0 1]. Further investigations are necessary in the material PZT-BNL + 3% PbO, concerning the presence of the pyrochlore phase, that could explain the lowest value of k_P.

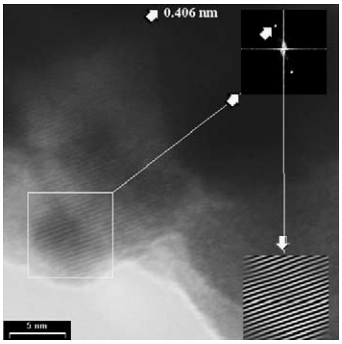

Fig. 6. HRTEM image on multidomain crystal (PZT-BNL material, sintered at 1280 °C).

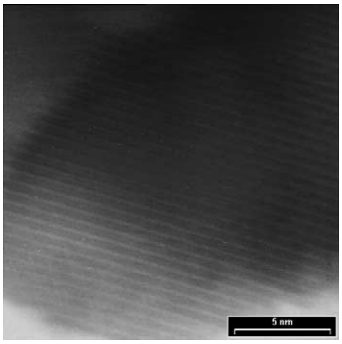

Fig. 7. Medium resolution TEM micrograph that reveals nano-domains in the PZT-BNL material.

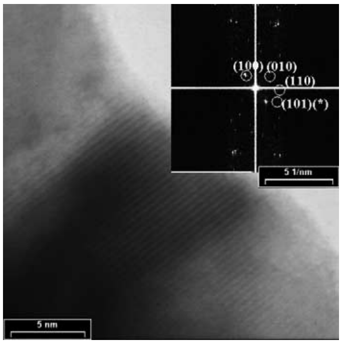

Fig. 8. HRTEM image on the sample PZT-BNL + 1% PbO.

3.2. *The influence of the bimorph on the resonance of the ventilator*

The frequency response of the transducer resembles fairly well the usual lorenzian curve characteristic for medium damped oscillators. Indeed the width of the spectrum is 3.1 Hz at 3 dB under the peak, which corresponds to a mechanical Q number of about 16. The emf response is fairly linear which reinforces the assumption that we find ourselves in the linear domain of the transducer. Of a special interest is the plot of Fig. 4, which suggests that, at least in the measured domain,

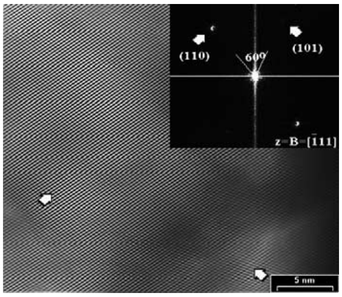

Fig. 9. HRTEM image presenting a single domain oriented along [−1 1 1] axis of tetragonal structure of PZT-BNL + 3% PbO.

there is no significant dependence between the resonance frequency and the linear dimensions of the ceramic bimorph. This allows a great simplification in the modeling of the ventilator: the metallic blade can be considered as an oscillator per se, driven by some external driver (the bimorph) and it is it which establishes the resonance of the whole resonator. In order to verify this assumption, we consider the free part of the metallic blade as being a particular case of a lateral oscillating bar one end clamped and the other end free. The equation of the motion of such a bar[6] is:

$$\frac{\partial^2 u}{\partial t^2} + k^2 b^2 \frac{\partial^4 u}{\partial x^4} = 0 \tag{1}$$

The boundary conditions for a clamped end is:

$$u(0) = 0 \tag{2}$$

$$\left|\frac{\partial u}{\partial x}\right|_{x=0} = 0 \tag{3}$$

and those for the free end is:

$$\left|\frac{\partial^2 u}{\partial x^2}\right|_{x=l} = 0 \tag{4}$$

$$\left|\frac{\partial^3 u}{\partial x^3}\right|_{x=l} = 0 \tag{5}$$

Here, b expresses the velocity of the compressional waves through the particular material the bar is made of, and k^2 is the moment of inertia of a transversal section through the bar relative to its central equilibrium line, versus its cross sectional area. In these conditions, the frequency of the bar is:

$$f = \frac{kb}{2\pi l^2} m^2 \tag{6}$$

For the a rectangular cross section:

$$k^2 = \frac{1}{12} t^2 \tag{7}$$

the metallic blade of the ventilator has the thickness t, 60 μm and the length l, 2.6 cm. The material of the blade is an alloy for which the velocity of the compressional vibrations is 3423 m/s, and m corresponding to the fundamental of the clamped-free mode is 1.875. The resulting frequency is 49.7 Hz, which is in a fairly good agreement with the experimental results (Fig. 2). The equation of motion for the blade of the ventilator is that of a rectangular bar, vibrating laterally, one end clamped and the other free. Thus, the shape of the blade will be described by a linear combination of trigonometric and hyperbolic sines and cosines:

$$\begin{aligned} u = {} & (\sin m + \sinh m)\left\{\cos\frac{mx}{l} - \cosh\frac{mx}{l}\right\} \\ & -(\cos m + \cosh m)\left\{\sin\frac{mx}{l} - \sinh\frac{mx}{l}\right\} \end{aligned} \tag{8}$$

4. Conclusions

A material with improved radial piezoelectric coefficient is prepared by partial substitution of the elements in a PZT (52/48) with Bi, Nb and Li ions. Enhanced piezoelectric properties are obtained by domains orientation after repeated poling, even the composition is shifted from the morphotropic phase boundary in the region of the tetragonal phase. The enhanced radial mode of a piezoceramic plate can be converted into flexural vibrations through a parallel rectangular bimorph. The vibrations are transmitted to an interstitial metallic blade which, driven at resonance displays large displacements of its free end. The movements of the free part of the blade can be successfully assimilated with the lateral vibrations of a bar, subjected to one end clamped and one end free boundary conditions, and driven by the ceramic bimorph. Thus, the resonance properties of the system are dictated mainly by the free part of the metallic blade. The experiments have proved that in the studied range, the ceramic bimorph plays an insignificant role in the establishment of the value of the resonance frequency. The only important factors in this are the geometrical (thickness and length) and acoustical (velocity of the compressional sonic wave in the material) properties of the free part of the vibrating blade. The shape assumed by the blade in its vibration is given by the specific solution of the equation of movement for the lateral vibrating bar.

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