High-Energy Density Piezoelectric Phase for ME Composites Energy Harvesters

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Abstract

One of the most important factors of controlling the magnetoelectric coefficient is high-energy density of piezoelectric phase in ME composites for energy harvesting. Optimal piezoelectric material for vibration energy converters is characterized by the highest magnitude of product of the piezoelectric voltage constant (g) and the piezoelectric strain constant (d). Single phase piezoelectric materials never have large value of both constants at the same time. The proposition for obtaining large magnitude of d*g has been presented as a creation of spatially graded structure from 2 materials with high value of both parameters. Experimental investigation of PZT planar graded structure was conducted to identify the correlation between composition, microstructure, and property. The optimization was conducted in terms of magnetoelectric coefficient (mV/cm·Oe) with supporting microstructural, structural and piezoelectric characterization.

Keywords
Functionally Graded Materials; Magnetoelectric Effect; PZT

1. Introduction

Energy harvesting has attracted much interest in the research community due to an intense development of such commercial devices as a power supply in large number of battery-less applications such as low-power wireless sensor networks [1], low energy consumption electronic or remote controllers [2] and miniaturized electromechanical systems (MEMS) [3]. This increasing attention is also visible in the quickly rising number of excellent
review articles that have been published on this topic [456]. At the same time, several applications have been projected for the mass scale energy harvesters for roads, railways and pedestrian zones as well as many more civilian and defense devices [4].

High power density of 300 μW/cm² that can be achieved in piezoelectric generators converting energy from mechanical vibrations is the most attractive alternatives for solar energy sources in indoor applications, where the energy density dramatically drops to 10-20 μW/cm² from 15000 μW/cm² of outdoor conditions level [4]. Consequently, from large number of different implementation ideas, the most commercial application of vibration harvesters is to power the dense wireless sensor nodes in buildings, cars and for health monitoring, where usually the most expensive is a supplying power part due to the necessity of wiring and batteries replacing [4]. Additionally in many places with limited access battery replacement operations may be restricted by the infrastructure.

Optimal piezoelectric material for vibration energy harvester is characterized by the highest magnitude of product of the piezoelectric voltage constant (g) and the piezoelectric strain constant (d) [49]. Among all piezoelectric materials there are two contradictive cases with extreme values of mentioned parameters: piezoelectric polymer PVDF with $g_{33} = 286.7 \times 10^{-3}$ m²/C but $d_{33} = 33$ pC/N and relaxor piezoelectric single crystals PMN – 33%PT with $d_{33} = 2523$ pC/N but $g_{33} = 27 \times 10^{-3}$ m²/C [11]. Nevertheless, the synthesis of single crystal and polymer in one volume is too challenging at the moment. The presented experimental results indicate, that the voltage coefficient of PMN-PT is not superior to PZT ceramics (20 - 27 × 10^{-3} m²/C) thus, it would appeared not to be particularly beneficial to use expensive PMN-PT single crystals for energy harvesting. Consequently, for mass applications, the most important focus is on improving the properties of polycrystalline ceramics. In this paper, the author presents the implementation of graded structure strategy idea for synthesis of high-energy density materials from two PZT ceramics with extremal values of d and g parameters.

2. Experimental section

2.1. Piezoelectric Graded Structure Synthesis

In a first step, commercial piezoelectric ceramics powders were chosen according its performance and prepared to solid-state reaction, namely: K2 synthesized powder, with the highest value of piezoelectric voltage constant (g) (CERAD company Warsaw, Poland) and S1 synthesized powder, with high value of the piezoelectric strain constant (d) (CERAD company Warsaw, Poland). The same amount of mentioned powders (2x50g), were axially pressed under 10 MPa pressure into pellets with outer diameter of 10 mm and inner diameter of 6 (Fig 1a). The compacted pellets were subsequently sintered at 1260 °C for 2 h in closed alumina crucible in lead and zirconia rich atmosphere (PbZrO3 + ZrO2).

Figure 1. PZT ceramic powder compacts with a gradient of chemical composition (a) and final K2 → S1 graded ceramics structure after sintering (b).

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2.2. Piezoelectric Graded Microstructure Analysis

After the graded sample preparation, the microstructure was investigated by SEM (Vega Plus 5136MM Tescan). Figure 2 gives a typical SEM image, along with the corresponding separated areas of S1 PZT ceramics presented in Figure 2a, and K2 PZT ceramics visible in Figure 2b, whereas Figures 2c and 2d revealing microstructures at area of the coexistence of both compositions in the fired graded sample. At the first look it visible that optimal sintering temperatures slightly differs for both materials because it is visible lack of distinctive grain boundaries in the case of K2 ceramics (Fig. 2b), that indicate start of the melting process. Similar problems with boundaries indication is presented in figure 2c where at the bottom part one can see the slightly visible gaps between K2 grains whereas in upper part well revealed borders of S1 ceramics are presented. Finally Figure 2d shows also fragment with sharply outlined grains from S1 ingredient and lack of grain edges in dark adjacent parts.

![Figure 2](image_url)

**Figure 2.** Morphologies of different sections in the fired graded structure of PZT S1 (a) PZT K2 (b) and SEM images of common section of S1 and K2 (c) and additional fragment of distinctly visible grains from common section (d).

2. XRD Structure Analysis of Piezoelectric Graded Samples

The phase composition of the sintered graded structures was analyzed by X-ray diffraction technique (PANalytical X’Pert Pro Multipurpose Diffractometer) with a Cu Kα source. The 2θ sweep range was from 5 to 80 degrees, with a step of 0.02. The Rietveld refinement method was used for estimation of unit cell dimensions applying Scherrer’s equation. To evaluate changes of the XRD diffraction peaks heights a standard PDF database was utilized. XRD patterns of both different sections in the fired sample (S1-a, K2-b) are shown in Fig. 3. The
tetragonal P4mm and rhombohedral R3c phases were identified in S1 and K2, that indicate the investigated materials belong to morphotropic area with coexistence of two mentioned structures. However there is only a small amount of R3c in S1 but this fact probably is connected with highest value of piezoelectric coefficient (d) for this particular unit cell shape, whereas more shifted towards the center of this area K2 is optimized for higher piezoelectric voltage constant (g). Lattice parameters for P4mm structure were equal for K2: a=b=4.0592(2), c=4.1158(2), whereas for S1 a=b 4.0216(3), c=4.1286(4) so that the calculated values confirms that unit cell become less tetragonal for K2 sample.

Figure 3. XRD patterns of different sections (S1–a) and (K2–b) in the fired graded PZT composite.

3. Piezoelectric coefficients measurement

An impedance frequency spectrum was measured using Agilent 4294A impedance analyzer in the frequency range from 100 kHz to 1 MHz for piezoelectric parameters evaluation using the resonance/antiresonance method \(^\text{[12]}\). The samples were poled in 120 °C for 10 minutes under the field of 3 kV/mm prior testing procedure.

The evaluated piezoelectric parameters value are presented in Table 1. The calculated data exhibit distinct improving tendency: as for planar electromechanical coefficient \(k_p\), graded structure significantly improved the value in 34 % but the most significant is the increase of \(g_{31}\) factor in 40 % to the value that is not present in commercially offered PZT ceramics. Generally in scientific laboratories to achieve such level of \(g\) advanced technologies must be implemented or methods that induce textured ordering in PZT ceramics like for example uniaxial hot pressing or extrusion techniques. This experiment proved that there is possible to achieve better piezoelectric performance by implementation conventional Mixed Oxide Method (MOM) with creation of spatially graded structure consisting of materials with extremal values magnitude piezoelectric voltage constant (g) and strain constant (d).

<table>
<thead>
<tr>
<th>Sample</th>
<th>(k_p)</th>
<th>(d_{31}\times10^{12} \text{[C/N]})</th>
<th>(g_{31}\times10^{-3} \text{[m²/C]})</th>
</tr>
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<tbody>
<tr>
<td>S1</td>
<td>0.31</td>
<td>47</td>
<td>19.5</td>
</tr>
<tr>
<td>K2</td>
<td>0.22</td>
<td>32</td>
<td>24.8</td>
</tr>
</tbody>
</table>
4. Conclusions

The measurements catalogued in the presented paper reveal a complex picture of energy conversion phenomena in the spatially graded PZT ceramics used for more efficient energy harvesting:

1. As far as our results are concerned an simple idea of spatially graded structure manufactured with conventional Mixed Oxide Method lead to energy conversion improvement for piezoelectric energy converters.

2. Contrary to the previous expectation on the resonating structures it was proved, that the piezoelectric voltage constant (g) without any doubt ensure 40% better energy transformation in the graded type of resonator, whereas the piezoelectric strain constant (d) value slightly decrease (6%), but the product property g*d is higher anyway.

3. As a final remark drawn from demonstrated experiment in which one can see increasing value of one piezoelectric parameter but decreasing the other one, that the implemented methods prove, that efficiency change mechanism is more complex and not fulfill simple analytical models, so that only practical examination can be effectively used for applications conclusions.

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References


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