



You have downloaded a document from  
**RE-BUŚ**  
**repository of the University of Silesia in Katowice**

**Title:** Lead Free Ba0.85Ca0.15TiO<sub>3</sub> Piezoelectric Transformer for Energy Harvesting Application

**Author:** Lucjan Kozielski, Kamil Feliksik, Beata Wodecka-Duś

**Citation style:** Kozielski Lucjan, Feliksik Kamil, Wodecka-Duś Beata. (2017). Lead Free Ba0.85Ca0.15TiO<sub>3</sub> Piezoelectric Transformer for Energy Harvesting Application. "Materiały Ceramiczne" (Vol. 69, nr 2 (2017) s. 68-72).



Uznanie autorstwa - Użycie niekomercyjne - Bez utworów zależnych Polska - Licencja ta zezwala na rozpowszechnianie, przedstawianie i wykonywanie utworu jedynie w celach niekomercyjnych oraz pod warunkiem zachowania go w oryginalnej postaci (nie tworzenia utworów zależnych).



# Lead Free $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{TiO}_3$ Piezoelectric Transformer for Energy Harvesting Application

LUCJAN KOZIELSKI\*, KAMIL FELIKSIK, BEATA WODECKA-DUŚ

Institute of Technology and Mechatronics, University of Silesia, 12 Żytnia St., 41-200 Sosnowiec, Poland  
\*e-mail: lucjan.kozielski@us.edu.pl

---

## Abstract

Piezoelectric Transformers are utilized to boost the conversion of mechanical vibration energy into electrical power with considerable potential in Energy Harvesting applications. Nowadays however, the critical challenge that need to be addressed is the use of lead free materials for their construction. The other requirements include the high conversion ratio, small size and reasonable power density. This work, for the first time, proposes implementation of the lead free  $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{TiO}_3$  material for a piezoelectric transformer that is designed for a vibration energy collection device.

**Keywords:** Energy Harvesting, Piezoelectric effect, Piezoelectric transformer, Ferroelectric properties

## BEZOŁOWIOWY TRANSFORMATOR PIEZOLEKTRYCZNY $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{TiO}_3$ DO ZBIERANIA ENERGII WIBRACYJNEJ

Transformatory piezoelektryczne wykorzystywane są w celu zwiększenia efektywności konwersji energii drgań mechanicznych w energię elektryczną z dużym potencjałem w zastosowaniach do zbierania energii z otoczenia. Obecnie jednak kluczowe wyzwanie, które należy rozwiązać, polega na wykorzystaniu bezzłowiowego, ceramicznego materiału piezolektrycznego do jego budowy. Pozostałe wymagania obejmują wysoki współczynnik konwersji, mały rozmiar i rozsądna gęstość mocy. Praca ta po raz pierwszy proponuje zastosowanie bezzłowiowej ceramiki  $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{TiO}_3$  w transformatorze piezolektrycznym, zaprojektowanym do urządzenia do zbierania energii wibracyjnej.

**Słowa kluczowe:** zbieranie energii, efekt piezolektryczny, transformator piezolektryczny, właściwości ferroelektryczne

---

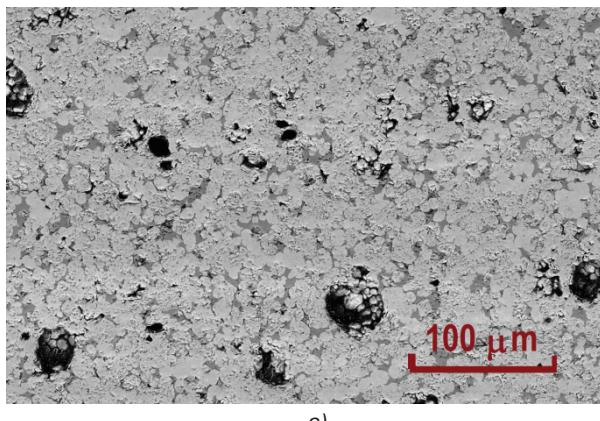
## 1. Introduction

Piezoelectric transformer (PT) is an important application of piezoelectric ceramics. It uses a mechanical vibration wave generated by the converse piezoelectric effect in the input part for generation of electrical voltage in the output part due to the common mechanical deformation (direct piezoelectric effect). For the Energy Harvesting, the most important property is that at resonance this device can amplify electrical voltage significantly increasing the conversion efficiency of captured environment energy [1]. Additional advantages include non-flammability, lack of electromagnetic noise generation and "embedded natural" insulation between input and output part, because all piezoelectric materials are dielectrics [2].

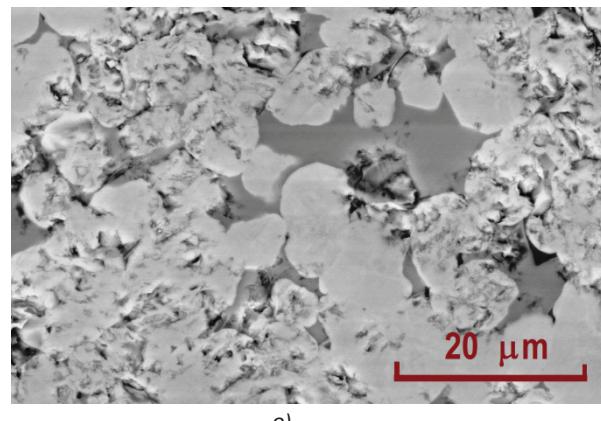
Advanced material science applications have recently the efficiency of capturing environment energy and transforming them into electrical power significantly increased [3, 4]. Additionally, huge progress in MEMS and microprocessor technology has significantly lowered their energy consumption [5]. In connection with both facts, these developments dynamically create a big interest in batteryless and wireless applications that utilize the energy harvesting for powering electronic devices. The latest technical solutions became

nowadays the effective technology for self-powered wireless networks and sensors [6]. The most attractive advantage in such an implementation is that those devices are completely autonomous without any need of maintenance and with not limited lifetime [7]. The next new interesting Energy Harvesting application area of PT's is connected with other EH technologies. Frequently used harvesters based on magnetoelectric (ME) and thermo-electric effects (TEG) provide the DC voltage lower than the classical threshold voltage of semi-conductors (<100 mV) so that they cannot then be stepped-up by classical transistor-based electronics. The start-up resonant oscillator converters are usually used to start at voltages as low as 10 mV to 100 mV, but they suffer from bulky magnetic transformers [8]. Piezoelectric transformers (PT's) are a good alternative to magnetic ones as they present much higher voltage gain, smaller size, and superior power density [3].

So far, the PZT ceramics played a dominant role in vibration piezoelectric transformers due to their excellent piezoelectric properties [9]. However, the significant environmental pollution arises during disposal of PbO-contaminated PZT ceramics. Consequently, the barium titanate ( $\text{BaTiO}_3$ ) materials, as the important lead-free piezoelectric ceramics, are attracting considerable attention [10]. The partial



a)



a)

Fig. 1. SEM images of polished  $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{TiO}_3$  samples under two different magnifications: a) general view and b) details of grain morphology.

substitution of Ba by Ca in the  $\text{BaTiO}_3$  solid solution results in an increase of the piezoelectric properties [11]. Therefore for the first time, the lead-free  $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{TiO}_3$  ceramics was implemented into the piezoelectric transformer structure for energy harvesting what described in this paper.

## 2. Experimental

$\text{Ba}_{0.85}\text{Ca}_{0.15}\text{TiO}_3$  (BCT) composition was prepared from stoichiometric amounts of high purity  $\text{TiO}_2$ ,  $\text{BaO}$  and  $\text{CaO}$  oxides (Aldrich, 99.99%) and milled in a planetary mill (RETCHE PM400) for 8 hours. All the component powders were subsequently pressed into cylindrical pellets that were next calcinated in an alumina crucible at 950 °C for 3 h. The obtained samples were crushed and milled again for 24 h to finally achieve reduction in the average grain size down to ~2  $\mu\text{m}$ . At the last stage, the resultant powder was compacted into disk-shaped pellets of 10 mm in diameter and 1 mm in height, and cold isostatically pressed at 2 GPa for 10 minutes. The samples were finally sintered at 1400 °C for 2 hours in air.

XRD diffraction patterns were recorded using an XRD PANalytical X'Pert Pro Multipurpose Diffractometer. The wide-angle scan from 5° to 80° was done with a step width of 0.02° (CuK $\alpha$ -radiation). For phase composition identification of the  $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{TiO}_3$  material, a quantitative analysis was performed by the Rietveld refinement method based on the respective structural models [12]. The dielectric permittivity measurements vs. temperature were carried out on heating by using a QuadTech 7600 Plus Precision LCR Meter. The obtained BCT samples microstructure was acquired by Hitachi S-4700 SEM.

Finally, both surfaces of the disk-shaped samples were coated with Ag epoxy paste (Electrodag 5915, Acheson Colloids Co. (Henkel), Germany) to ensure the electrical contact. All the samples were polarized at room temperature for 10 min at electric field of 3 kV/mm. The large signal polarization and strain hysteresis as a function of applied electric field was recorded at 0.1 Hz. Small signal stimulus (100 V at 0.1 Hz) was applied, and the displacement was measured with a laser interferometer. The piezoelectric coefficient was measured with a quasistatic  $d_{33}$ -meter (YE 2730a, Sinocera, China) at 110 Hz.

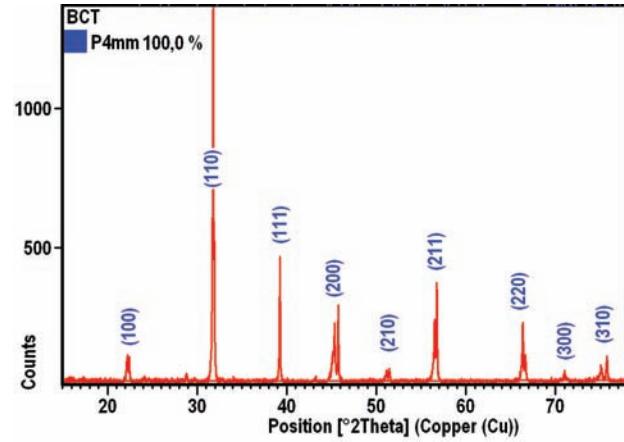


Fig. 2. XRD diffraction patterns of  $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{TiO}_3$  ceramics.

## 3. Results and discussion

### 3.1. Microscopy investigations of the sample surfaces

Fig. 1 shows the SEM images of polished surfaces of the  $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{TiO}_3$  samples under two different magnifications. Well developed grain morphology is clearly visible from the comparative analysis between the corresponding images obtained under the variant magnification. The surface image of the BCT sample reveals scattered distribution of shapes and sizes of crystallites being characteristic for the Mixed Oxide Method (MOM).

### 3.2. Phase composition identification by X-ray diffraction

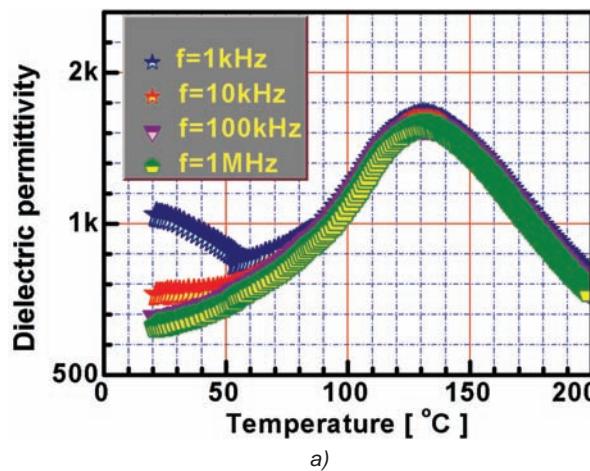
Fig. 2 shows the Rietveld refined XRD diffraction patterns of the  $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{TiO}_3$  samples. The presented diagram shows the formation of perovskite phase with tetragonal symmetry as it lies next to the  $\text{BaTiO}_3$  rich end in the barium-calcium titanate solid solution. The XRD analysis confirms the formation of all the reflections expected for the tetragonal P4mm space group. In addition, a peak is distinctly visible, splitting behaviour of (200) reflection which typically indicates the tetragonal phase of  $\text{BaTiO}_3$ .

### 3.3. Dielectric properties

The complex dielectric permittivity was studied in the temperature range from 20°C to 200°C and frequency one of 1 kHz – 1 MHz. Figs 3a and 3b present the temperature dependence of dielectric constant,  $\epsilon_r$ , and dielectric loss tangent,  $\tan \delta$ , of the obtained BCT sample. A phase transition temperature from the ferroelectric state to the paraelectric one was recorded at 130°C for this BCT sample. There was no frequency dispersion observed in the measured frequency range that confirms high homogeneity of the obtained ceramics. A dielectric loss tangent value is not higher than 0,5 in the whole measured temperature range.

### 3.4. Ferroelectric properties

Figs 4a and 4b show polarization and uniaxial displacement as a function of applied electric field for the obtained  $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{TiO}_3$  material. After identification of ferroelectric phase in the BCT sample, there is no surprise that the P-E loop presents the ferroelectric-like shape as expected for barium calcium titanate ceramics (Fig. 4a). Small displacement of 60 nm at the electric field of 10 kV/cm was similarly recorded that confirms the piezoelectric behaviour of the obtained sample (Fig. 4b).

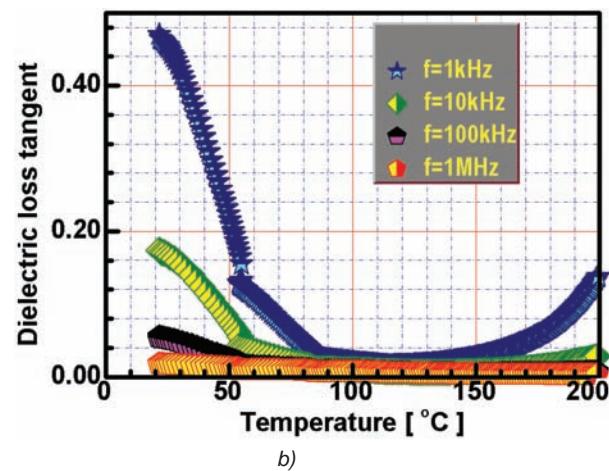


a)

### 3.5. Piezoelectric coefficients evaluation

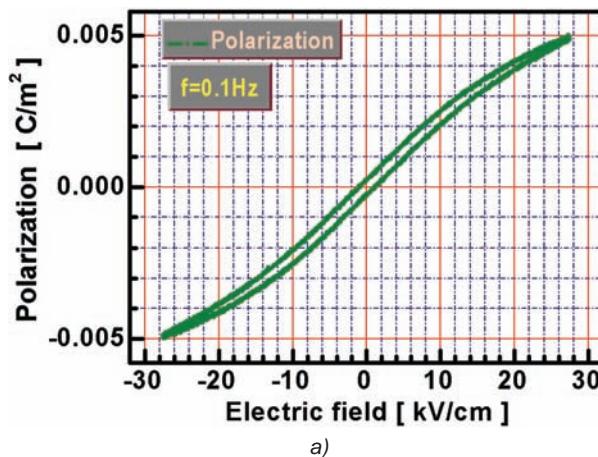
The recorded extreme values of the impedance modulus and phase for the first and second resonant frequency are presented in Figs 5a and 5b, respectively. The calculated piezoelectric parameters of the homogeneous BCT discs, shown in Table 1, were measured according to the standard method (EN 50324–2) [13]. A quasi-static “Berlincourt technique” was additionally implemented for the direct evaluation of  $d_{33}$  ( $d_{33}$ -meter) [14]. The measured  $d_{33}$  of the obtained BCT ceramics is significantly less than that of lead competitor PZT but it is well known that piezoelectric coefficients of lead free materials are smaller compared with those of bulk PZT.

The BCT discs were covered with ring-dot electrodes, and used for the piezoelectric transformer. The experimental data of gain and efficiency vs. frequency are shown in Figs. 6a and 6b, respectively, for the designed transformer for various load conditions ( $Z_L \approx 1 - 50 \text{ k}\Omega$ ). It is clearly seen that the theoretical expectation about the lower transformation ratio in the lead free ceramic is confirmed. This explanation is further supported by the measured efficiency for the homogeneous sample; its value is close to 14% (see Fig. 6b), when there are the low load conditions only.

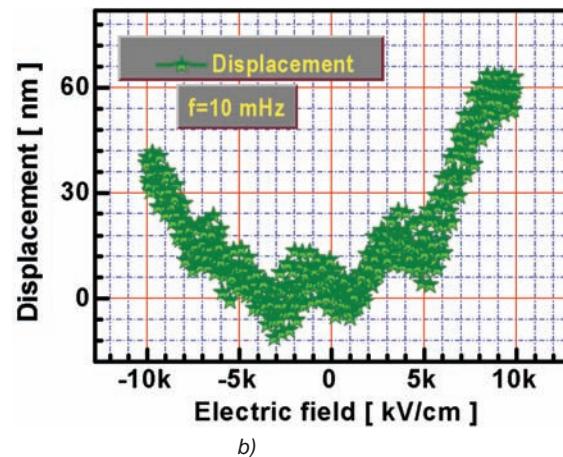


b)

Fig. 3. Dielectric permittivity (a) and dielectric loss tangent (b) temperature dependencies of  $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{TiO}_3$  ceramics.



a)



b)

Fig. 4. BCT ceramics hysteresis loop (a) and field-induced displacement (b) (with  $\pm 10 \text{ kV/cm}$ , 0.1 Hz driving field at room temperature and sample thickness of 1 mm).

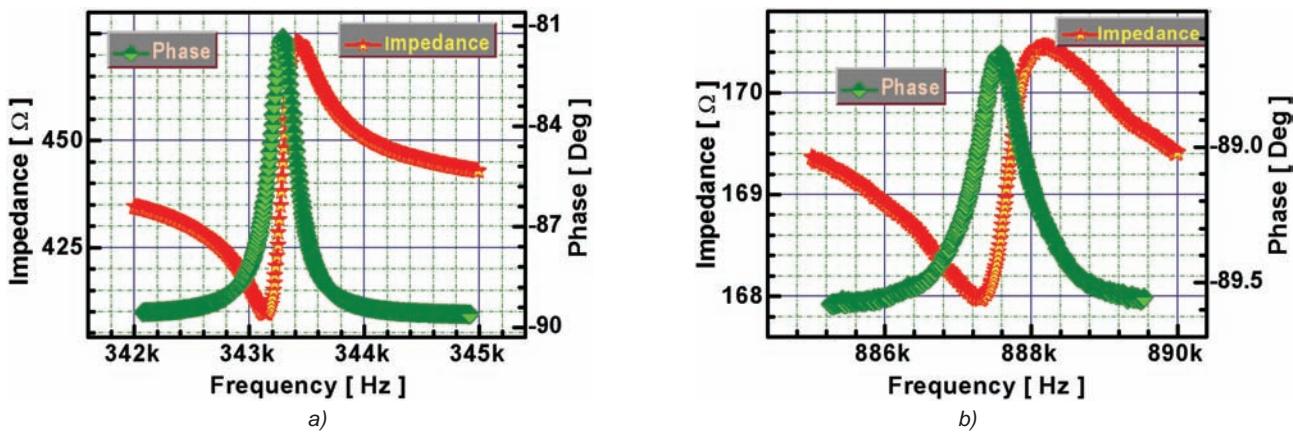


Fig. 5. Recorded extreme values of impedance modulus and phase for the first (a) and second (b) resonant frequency.

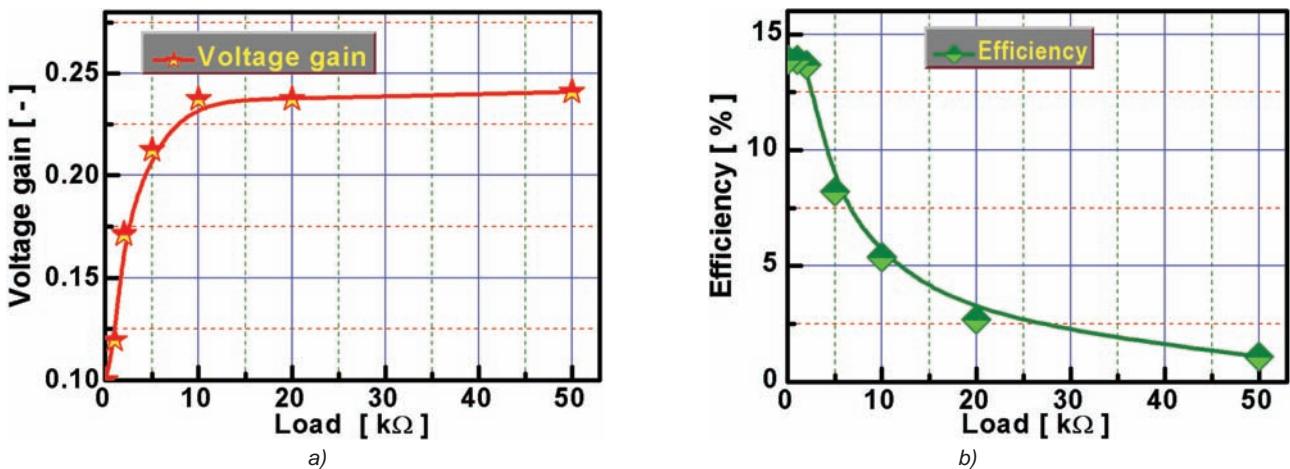


Fig. 6. Experimental data of gain (a) and efficiency (b) vs. frequency for various load condition ( $Z_L \approx 1 - 50 \text{ k}\Omega$ ) for the designed BCT transformer.

Table 1. Piezoelectric parameters values of the obtained BCT sample.

Parameter	Definition	Value	Unit
	Longitudinal permittivity at constant stress $T$	337	[F/m]
$Q_M$	Mechanical quality factor	3076	[ $\cdot$ ]
$k_{31}$	Transversal coupling factor	0.03	[ $\cdot$ ]
$k_p$	Planar coupling factor	0.044	[ $\cdot$ ]
$d_{33}$	Longitudinal piezoelectric coefficient	8	[pC/N]
$d_{31}$	Transversal piezoelectric coefficient	5	[pC/N]

The maximum transformation ratio was recorded as low as 0.23 at 50  $\text{k}\Omega$  load for the implemented BCT ceramics. It is generally evident that the barium-calcium titanate ceramic transformer has about 10 times smaller transformation ratio and efficiency than its PZT based ring-dot counterpart [15].

#### 4. Conclusions

$\text{Ba}_{0.85}\text{Ca}_{0.15}\text{TiO}_3$  disk samples were obtained by the Mixed Oxide Method and prepared for lead free piezoelectric transformers.

Structural and electrical analysis was performed by SEM and XRD approach together with dielectric spectroscopy,

which proved the selection of the proper synthesis conditions.

The studies also showed weak effectiveness of the barium calcium titanate ceramics for manufacturing piezoelectric transformer for Energy Harvesting structures. The barium calcium titanate ceramic transformer has generally about 10 times smaller transformation ratio and efficiency than its PZT based ring-dot counterpart.

#### Acknowledgements

This research was supported by the National Centre for Research and Development, grant no. TANGO1/267100/NCBR/2015.

## References

- [1] Sebastian, T., Erhart, J.: Bar Piezoelectric Ceramic Transformers Working in Longitudinal Mode, *Ferroelectrics*, 486, (2015), 13–24.
- [2] Sebastian, T., Kozielski, L., Erhart, J.: Co-sintered PZT ceramics for the piezoelectric transformers, *Ceram. Int.*, 41, 8, (2015), 9321–9327.
- [3] Mateu, L., Moll, F.: Review of energy harvesting techniques and applications for microelectronics, *SPIE VLSI Circuits and Systems II*, 5837, (2005), 359–373.
- [4] Heung Soo K., Joo-Hyong K., Jaehwan K.: A review of piezoelectric energy harvesting based on vibration, *Int. J. Precis. Eng. Man.*, 12, (2011), 1129–1141.
- [5] Cook-Chennault, K. A., Thambi, N., Sastry, A. M.: Powering MEMS portable devices - a review of non-regenerative and regenerative power supply systems with special emphasis on piezoelectric energy harvesting, *Adv. Mater. Res.-Switz.*, 17, (2008), 1–33.
- [6] Ulukus, S., Yener, A., Erkip, E., Simeone, O., Zorzi, M., Grover, P., Huang, K.: Energy Harvesting Wireless Communications: A Review of Recent Advances, *IEEE J. Sel. Area Comm.*, 33, (2015), 360–381.
- [7] Wan, Z. G., Tan, Y. K., Yuen, C.: Review on energy harvesting and energy management for sustainable wireless sensor networks, *Proc. of IEEE 13th Int. Conf. on Comm. Techn.*, (ICCT'11), (2011), 362–367.
- [8] Martinez, T., Pillonnet, G., Costa, F.: A 12 mV start-up converter using piezoelectric transformer for energy harvesting applications, *J. Phys.*, 773, (2016), 012028 1–5.
- [9] Heywang, W., Lubitz, K., Wersing, W.: *Piezoelectricity: evolution and future of a technology*, Springer Science & Business Media 2008.
- [10] Priya, S., Nahm, S.: *Lead-free piezoelectrics*, Springer Science & Business Media 2011.
- [11] Liu, W., Ren, X.: Large Piezoelectric Effect in Pb-Free Ceramics, *Phys. Rev. Lett.*, 103, (2009), 257602.
- [12] Rietveld, H. M.: A profile refinement method for nuclear and magnetic structures, *J. Appl. Crystallogr.*, 2, (1969), 65–71.
- [13] IRE Standards on Piezoelectric Crystals: Measurement on Piezoelectric Ceramics IEEE, New York, 1961.
- [14] Fei, L., Xu, Z., Wei, X., Jin, L., Gao, J., Zhang, C., Yao, X.: Evolution of transverse piezoelectric response of lead zirconate titanate ceramics under hydrostatic pressure, *J. Phys. D: Appl. Phys.*, 42, (2009), 095417 – 095424.
- [15] Erhart, J.: Bulk piezoelectric ceramic transformers, *Adv. Appl. Ceram.*, 112, (2013), 91–96.



Received 22 June 2017, accepted 19 July 2017.