Project: PN-III-P4-ID-PCE-2020-1988

Contract: PCE 168/2021

SCIENTIFIC REPORT

January-December 2021

Engineering of lead-free porous ceramic materials for piezo-, pyroelectric sensors with energy harvesting applications

(acronim: EnginPOR)

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Year I (2021) - Summary

In this first stage, the activities from the project implementation plan which have been accomplished are:

- ***A1.1-3 1) the development of combined models for the simulation of porous microstructures and the estimation of their role on the piezoelectric response; 2) Study of the impact of electric field distribution on the dielectric, piezo / pyroelectric response, P (E) and tunability for different pore shapes (continued in 2022); 3) Design of piezo- / pyroelectric ceramic microstructures, using theoretical models, with improved FOM (continued in 2022).***
- ***A1.4-5 synthesis activities and microstructural characterization of powders based on solid solutions of BT doped in positions A and / or B of the perovskite cell which will be used as ferroelectric matrix, and the Pb-free porous ceramics obtained by the synthesis powders (continued 2022).***
- ***In the activity A1.6, the design and production of experimental devices for the detection, conversion, measurement of thermal and mechanical impulses for energy collection from different environments was performed.***
- ***A1.7 Coordination, management and dissemination of the results obtained.***

Scientific and technical description of the activities and results

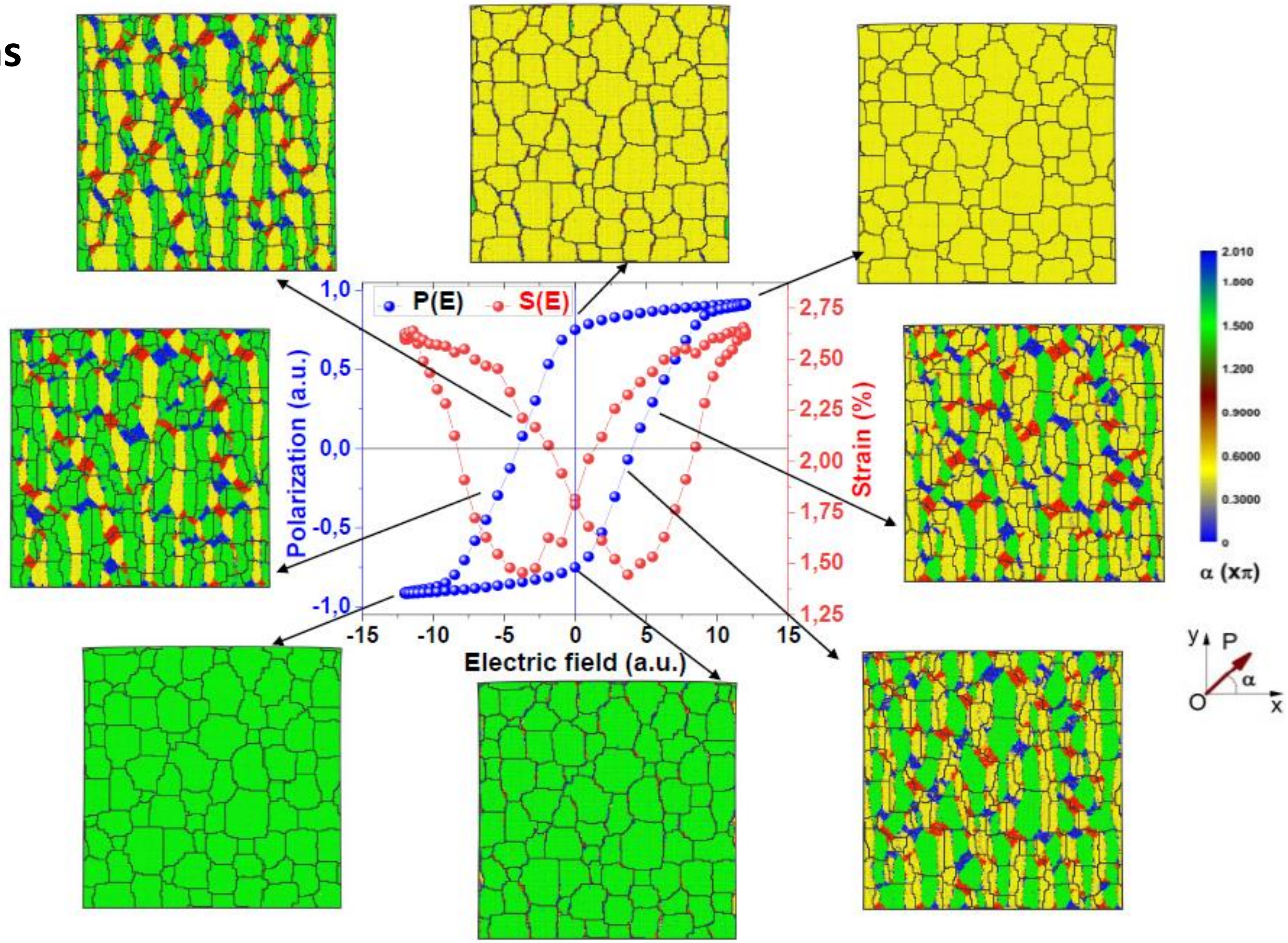
Year I - 2021

Design, preparation and microstructural characterization of Pb-free porous ceramics. Design and testing of experimental set-up for harvesting energy.

A1.1-3 Development of combined models for the simulation of porous microstructures and estimation of the piezoelectric response in porous materials; study of impact of electric field distribution on dielectric, piezoelectric response and P(E) properties (will be continue in 2022).

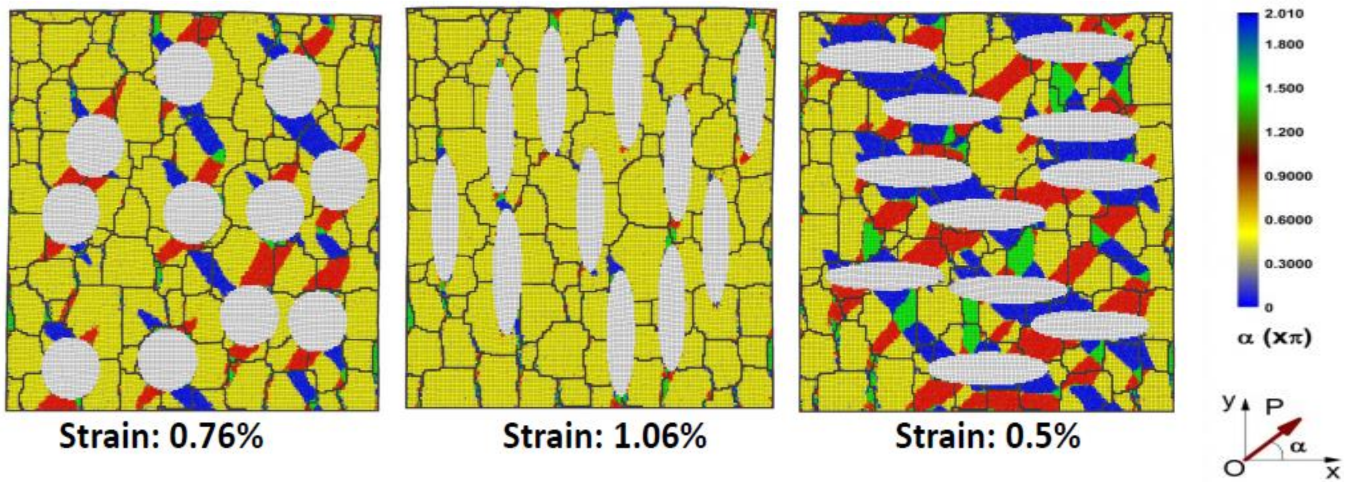
It was study the role of microstructure on dielectric, piezoelectric and ferroelectric properties in porous ceramic microstructures by using Monte Carlo Methods combined with Landau-Ginzburg-Devonshire theory.

- **Theoretical simulations results**

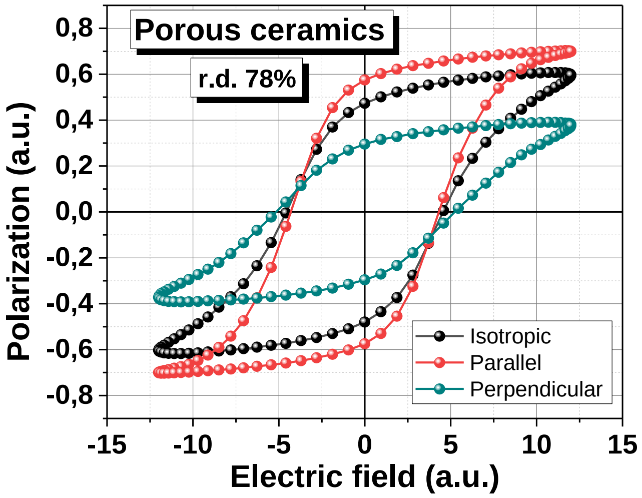


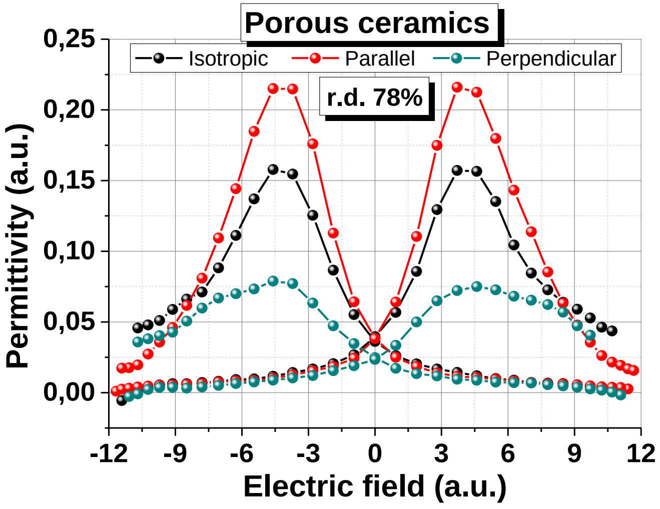
Domain structures (and local deformations), resulting from Monte Carlo simulations at different times of a complete hysteresis cycle, together with the hysteresis cycles of P(E) polarization and S(E) relative deformation calculated from the model in a dense microstructure.

- **Theoretical calculation and simulations results – in microstructures with 78% relative density with different shape of pores**



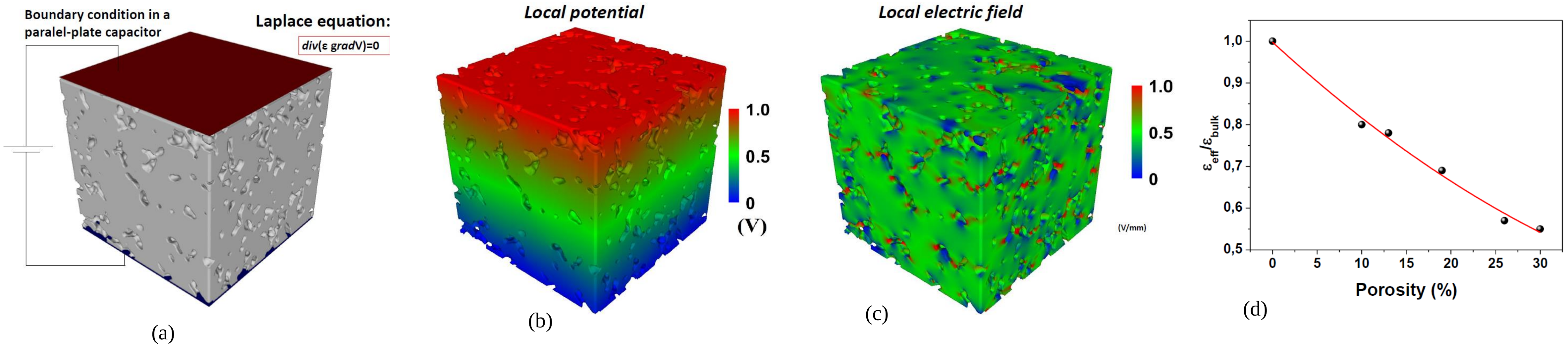
Domain structures for porous ceramics with the same density (22% relative porosity), if the configurations are: (a) isotropic (spherical pores), (b) with elongated pores oriented with a long parallel axis, (c) with elongated pores oriented with a long axis perpendicular to the direction of the applied electric field.





***P*(*E*) and a.c. tunability *ε*(*E*) calculated from Monte Carlo simulations in all three cases for a porous ceramic microstructure**

• Design of piezo- /pyroelectric ceramic microstructures, using theoretical models, with improved Figure Of Merit.
3D Finite Element Model (FEM) to determine the porosity dependence of isotropic permittivity.



(a) The porous microstructured considered in the simulations by taking into account the specific boundary conditions; (b), (c) The potential and the local field represented in the color scale; (d) Porosity dependence of effective permittivity.

Results AI.1-3:

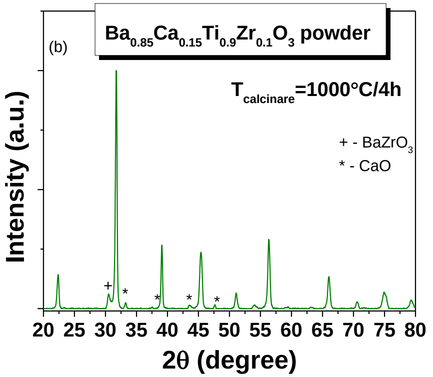
- **Developing of combined Monte Carlo and LGD models for monitoring evolution of ferroelectric domains, their displacement with and no applied electric field in order to estimate the ferroelectric P(E) and S(E) – piezoelectric response, in dense and porous microstructures;**
- **Estimation by theoretical simulation of the impact of electric field distribution on the P(E) and tunability in porous ceramic microstructures with different pore shapes;**
- **By using 3D FEM, it was shown that a relative porosity of ceramics of 10% leads to a decrease of the permittivity compared to that of dense ceramics to 80%, and for a relative porosity of 30%, the decrease of permittivity reaches 55% compared to that corresponding to the dense material.**

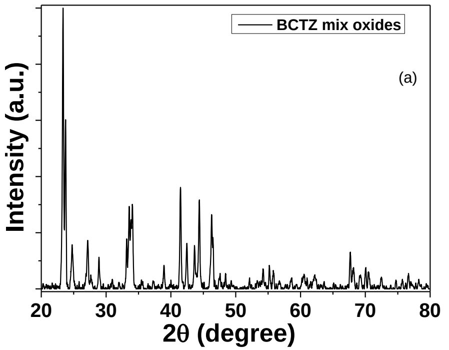
➢ *A1.4-5 Synthesis and microstructural characterization of powders based on BT-solid solution with single or double substitution for used as ferroelectric matrix. Production of Pb- free porous ceramics (with different types of pore connectivity) (will continue in 2022).*

At this stage it was prepared the ferroelectric composition of the **$Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ system** (the most important feature of this system is the existence of a triple C-R-T point in the phase diagram, which gives it superior electrical properties unlike other BT-based systems).

$$0.85BaCO_3 + 0.15CaCO_3 + 0.1ZrO_2 + 0.9TiO_2 \rightarrow Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3 + CO_2\uparrow$$

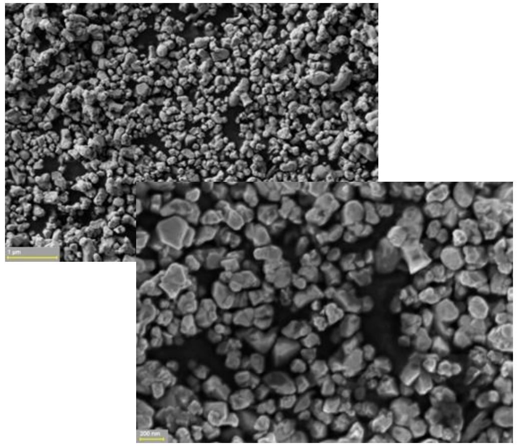
- **XRD – structural analysis**

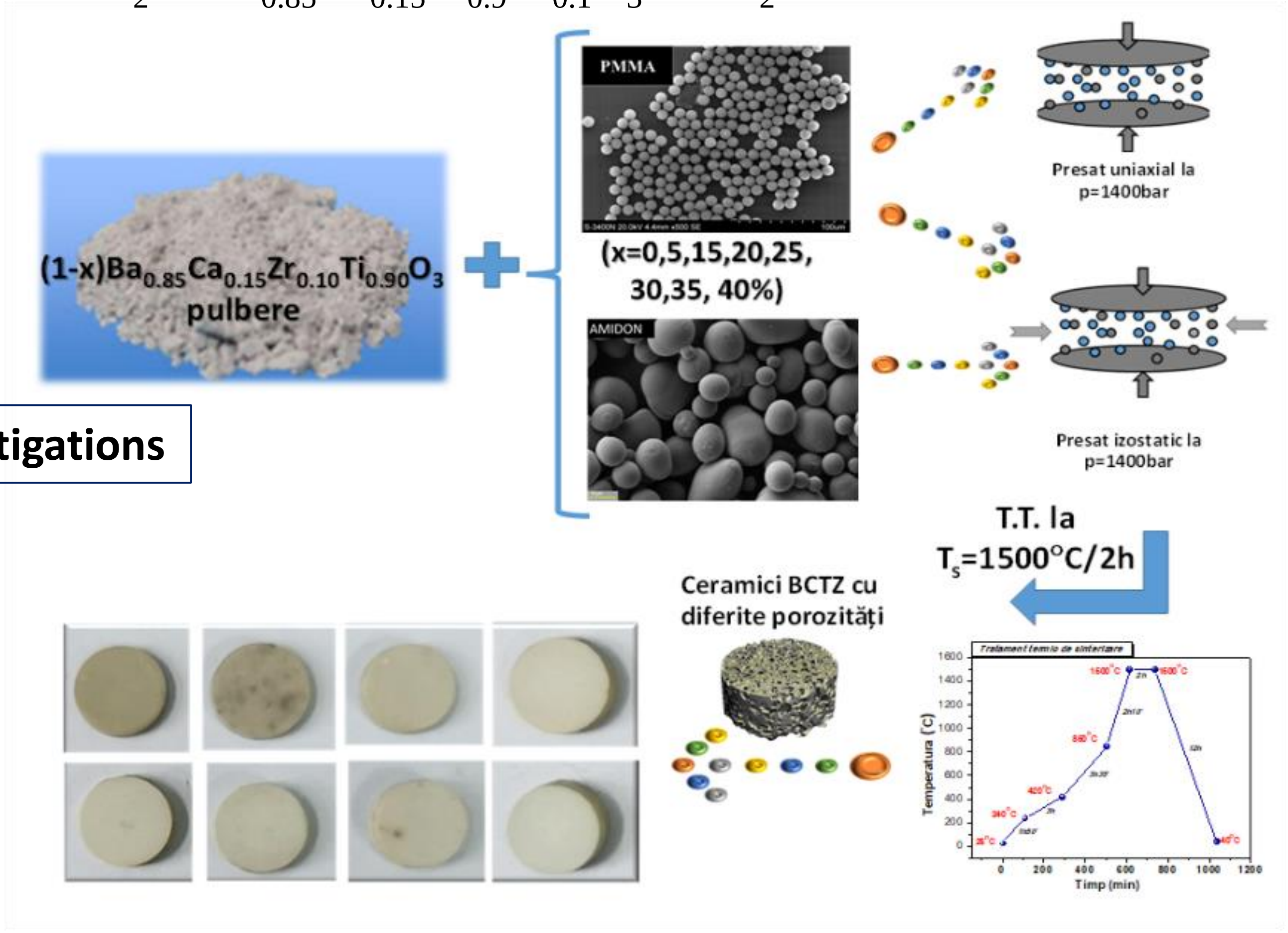




Pure phase of BCTZ calcinated powder

- **SEM – microstructural investigations**





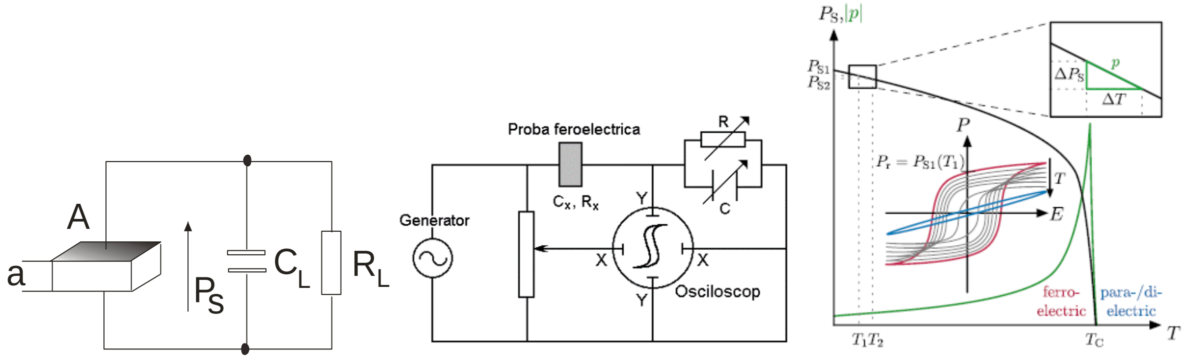
Results AI.4-5:

- **BT-based perovskite powders with the composition $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ (BCTZ);**
- **3 sets of porous BCTZ ceramics, with different degree of porosity, obtained by combination of BCTZ powder with different sacrificial materials (PMMA and starch);**

A1.6 Design and production of experimental set-ups for the detection, conversion, measurement of thermal and mechanical impulses for harvesting energy in different environments.

At this stage it was design and implement the experimental set-ups, techniques and measurement protocols for the detection, conversion and measurement of thermal and mechanical pulses for porous ceramic materials, in order to use them in devices for energy harvesting applications from different backgrounds.

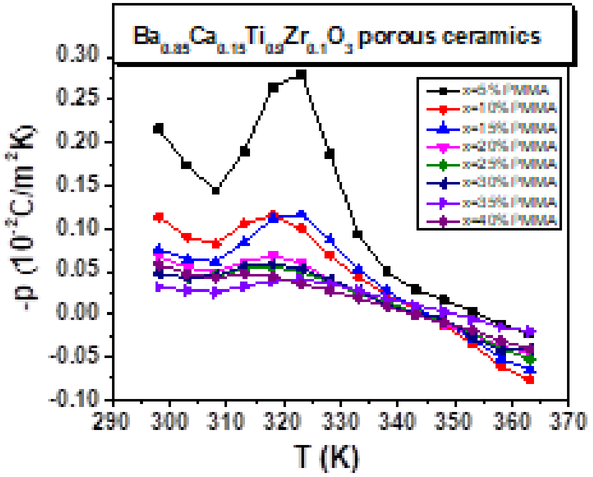
- **Experimental set-up for detection, conversion and measurement of thermal pulses - pyroelectric coefficient**



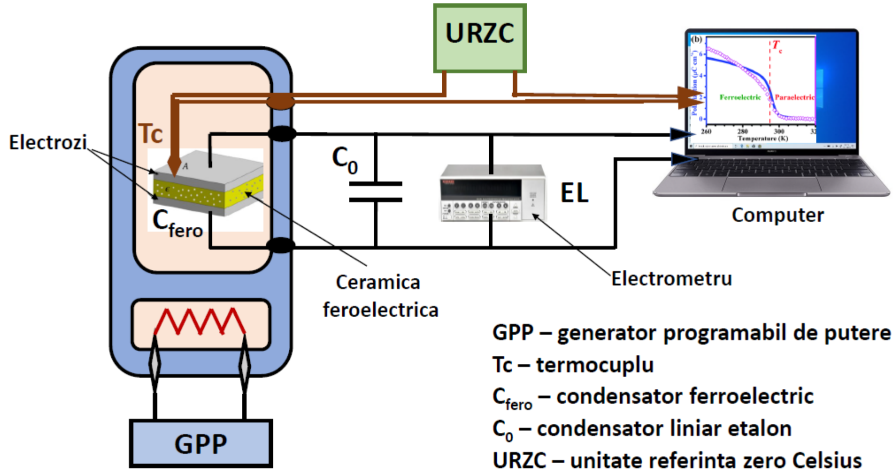
Schematic representation of circuits for pyroelectric measurements

$$p = \frac{\partial P}{\partial T}$$ - Pyroelectric coefficient

Results of pyroelectric coefficient for porous ceramics:



Schematic representation of experimental set-up for measurement of pyroelectric response

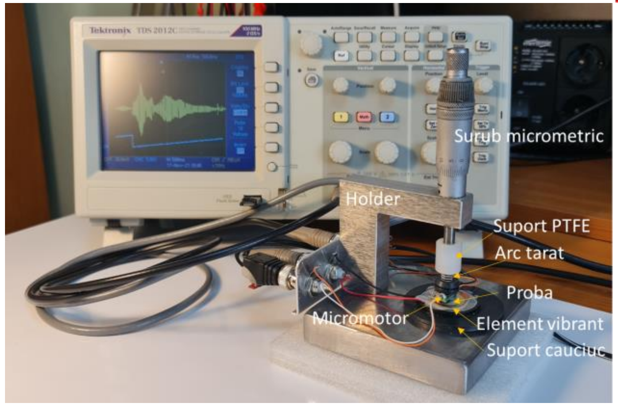


Results of pyroelectric measurements and tests depend:

- on poling strategy of the investigated samples;
- the rate of temperature variation at thermal depolarization from room temperature to Curie temperature;
- the size of the investigated samples.

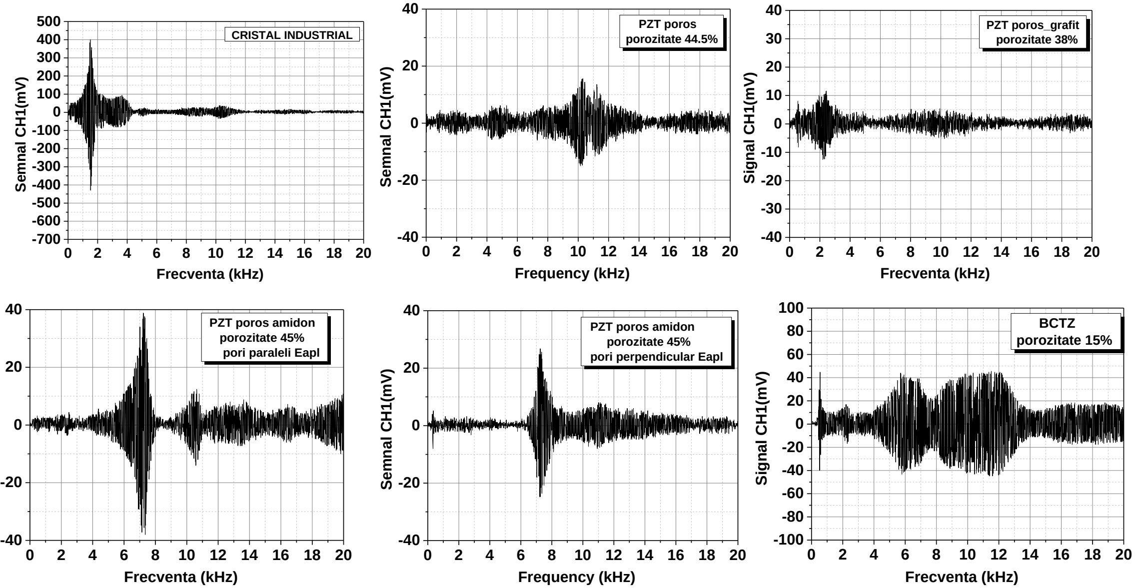
- *The sensitivity of the method depends on the heating rate of the sample and the specific heat of the material as well as the speed at which the thermal equilibrium is reached.*

- **Experimental set-up for energy harvesting by using mechanical stimulus and different frequencies**

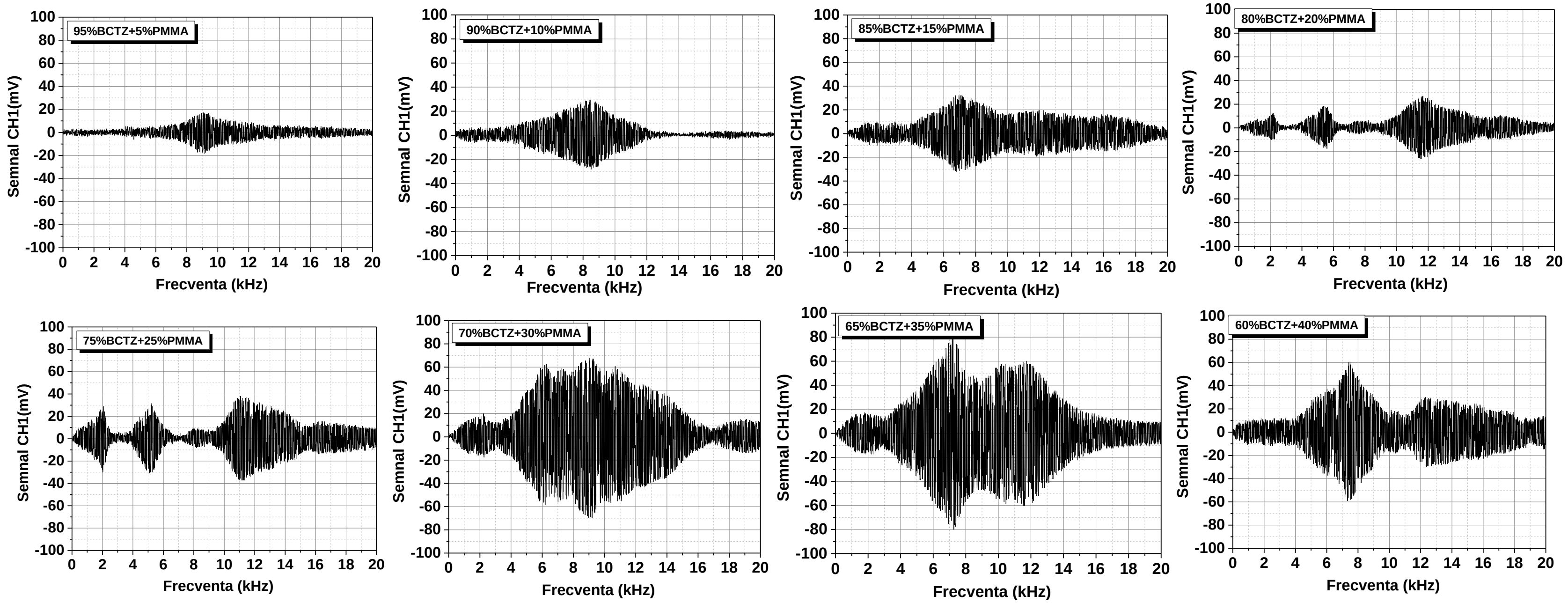


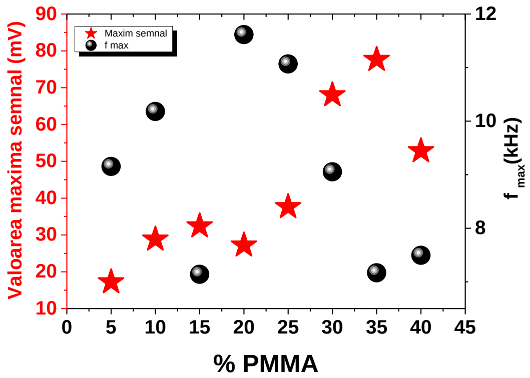
Set-up for determination and conversion of mechanical vibrations from piezoelectric materials

Results of piezoelectric measurements and tests on different dense and porous ceramics:



Results of piezoelectric measurements on BCTZ porous ceramics:

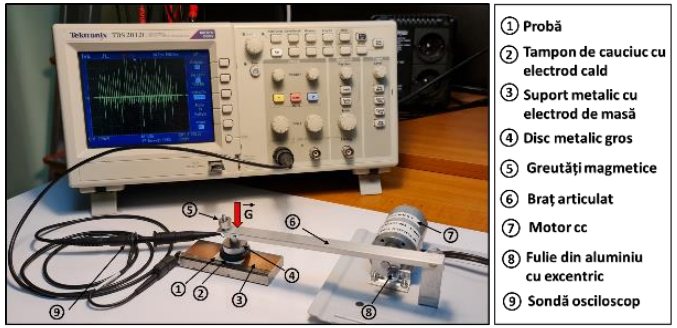


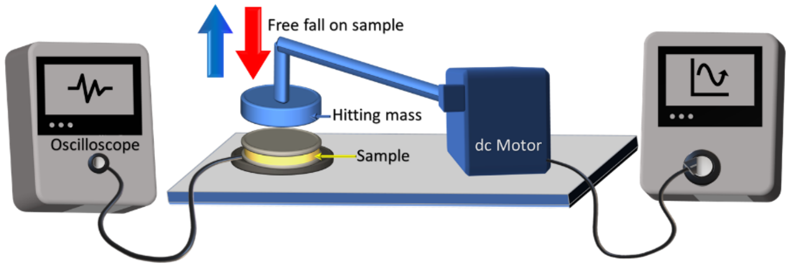


Results AI.6:

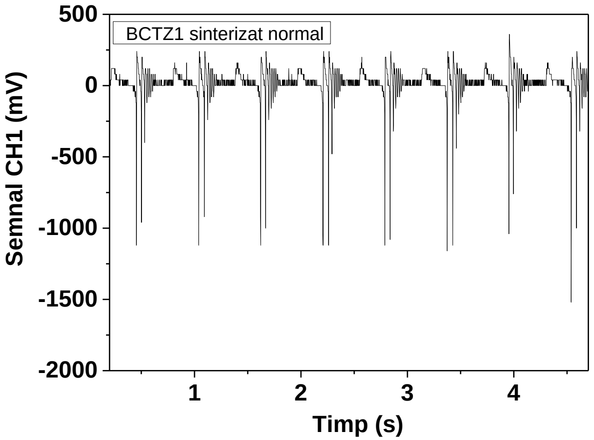
- The experimental set-up realised for measuring and testing the piezoelectric response has demonstrated and confirmed the beneficial effect of porosity for increasing the collected signal over a certain frequency range and finding the range of interest for energy conversion as *f*= 6 ÷ 10 kHz.

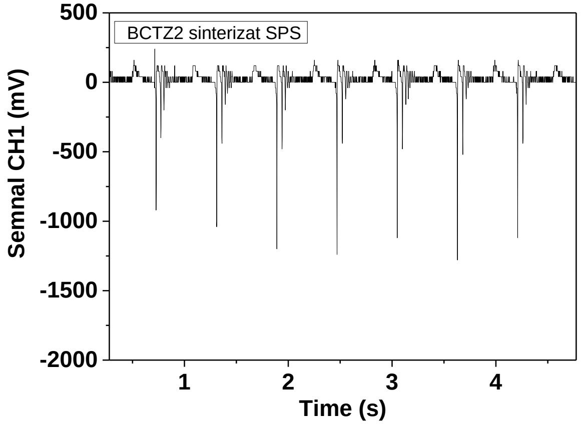
- **Experimental set-up for energy harvesting from mechanical stress on piezoelectric ceramics**





Results of test and calibration of energy piezoelectric harvesting set-up:





Results AI.6:

- The design experimental set-up has the ability to collect the electrical signal generated from the piezoelectric ceramics and to demonstrate their applicative potential as materials for energy harvesting applications.

➢ A1.7 Coordination, management, dissemination.

- It was realised the **web page of the project**: https://www.uaic.ro/enginpor/
- **1 published article**:

Modifications of structural, dielectric and ferroelectric properties induced by porosity in BaTiO3 ceramics with phase coexistence, Leontin Padurariu, Lavinia-Petronela Curecheriu, Cristina-Elena Ciomaga, Mirela Airimioaei, Nadejda Horchidan, Cipriana Cioclea, Vlad-Alexandru Lukacs, Radu-Stefan Stirbu, Liliana Mitoseriu, Journal of Alloys and Compounds 889, 161699 (2021) (ISI=5.316, Q1) in collaboration with PN-III-P1-1.1-TE-2019-1929 project;

- The scientific results were presented at **3 international conferences** – 6 presentations (invited, orals and poster):

1. *Design, synthesis and functional properties of porous BZT-BCT ceramics,* Cristina E. Ciomaga, Lavinia P. Curecheriu, Leontin Padurariu, George Stoian, Iwona Lazar and Liliana Mitoseriu, XV National Meeting on Electroceramics, 7- 9 July 2021, Vitoria-Gasteiz, Spain (https://cicenergigune.com/en/agenda/xv-national-meeting-electroceramics) **(oral presentation)**
2. *Room temperature phase superposition of barium titanate- based ceramics: modelling and experimental validation*, Leontin Padurariu, Nadejda Horchidan, Mirela Airimioaei, Lavinia Curecheriu, Cristina Ciomaga, Liliana Mitoseriu, XV National Meeting on Electroceramics, 7- 9 July 2021, Vitoria-Gasteiz, Spain (https://cicenergigune.com/en/agenda/xv-national-meeting-electroceramics) **(oral presentation)**
3. *Preparation and functional properties of $BaTiO_3$–based ceramics*, Nadejda Horchidan, Cristina Ciomaga, Lavinia Curecheriu, Liliana Mitoseriu, XV National Meeting on Electroceramics, 7- 9 July 2021, Vitoria-Gasteiz, Spain (https://cicenergigune.com/en/agenda/xv-national-meeting-electroceramics) **(oral presentation)**
4. *Effect of sintering on structural and electrical properties of $(Ba,Sr)(Zr,Ti)O_3$ ceramics for energy storage applications,* Cristina Ciomaga, Lavinia Curecheriu, Alexandru Lukacs, and Liliana Mitoseriu, 13th International Conference Processes in Isotopes and Molecules PIM 2021, 22-24 September 2021, Cluj-Napoca, Romania (http://pim.itim-cj.ro/pages/programme.html) **(poster presentation)**
5. *Effect of porosity on dielectric, ferroelectric and piezoelectric properties in $BaTiO_3$- based materials*, Cristina E. Ciomaga, Leontin Padurariu, Lavinia P. Curecheriu, Alexandru V. Lukacs, Nadejda Horchidan and Liliana Mitoseriu, 11th International Advances in Applied Physics & Materials Science Congress &Exhibition (APMAS), 17-23 October 2021, Oludeniz, Turkey (http://www.apmascongress.org/) **(invited presentation)**
6. *Exploiting local field inhomogeneity for tunning functional properties in ferroelectric based composites*, Leontin Padurariu, Lavinia Curecheriu, Cristina Ciomaga, Liliana Mitoseriu, 11th International Advances in Applied Physics & Materials Science Congress &Exhibition (APMAS), 17-23 October 2021, Oludeniz, Turkey (http://www.apmascongress.org/) **(invited presentation)**

- **On-line seminar Romania - Poland concerning effect of porosity on piezoelectric response in BCTZ ceramics.**
- **Purchases of equipment** : Freeze dryer ; Powder sieving machine; Vibration system - in a wide range of frequencies, High-performance computers, necessary for carrying out research and dissemination activities within the project.

All the activities of this I stage (2021) have been successfully completed.