Executive summary of the activities carried out during the implementation period

January 2021- December 2023

Project: Engineering of lead-free porous ceramic materials for piezo-, pyroelectric sensors with energy harvesting applications (acronim: EnginPOR)

PN-III-P4-ID-PCE-2020-1988 Contract: PCE 168/2021

Project Team:

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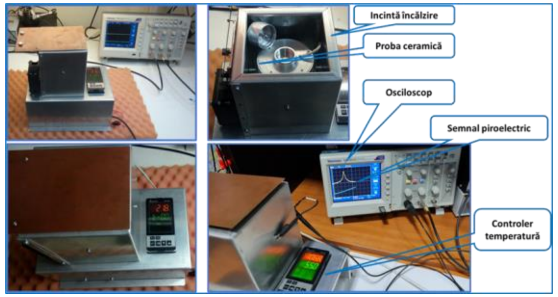
Aim of project

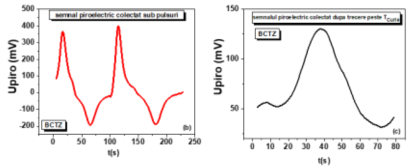
- ***to design, produce and test Pb-free porous ceramic piezo- and pyroelectric sensors with controlled microstructures in complex experimental devices for energy harvesting applications for a new generation of sensor devices.***

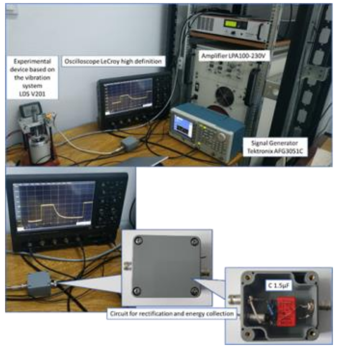
The project demonstrates a new concept based on the use of controlled porosity in ferroelectric ceramics as a tool to improve the factor of merit (FOM), by decreasing the electrical permittivity values and maintaining high piezo- and pyroelectric constants.

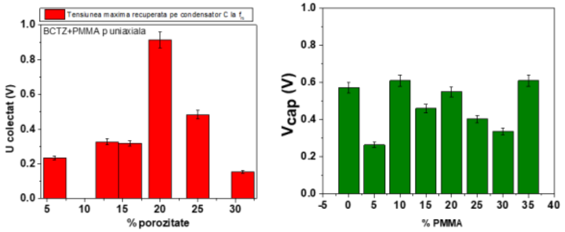
Project PN-III-P4-ID-PCE-2020-1988, Contract: PCE 168/2021

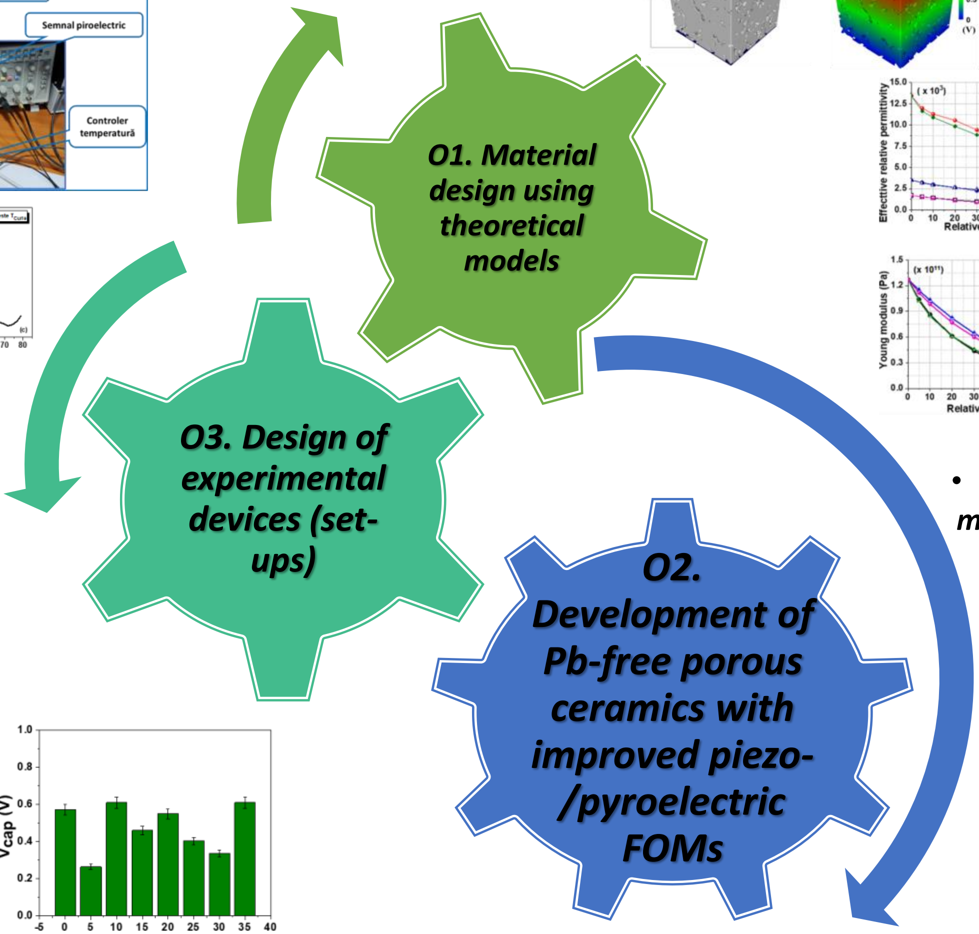
- *Experimental Set-ups*



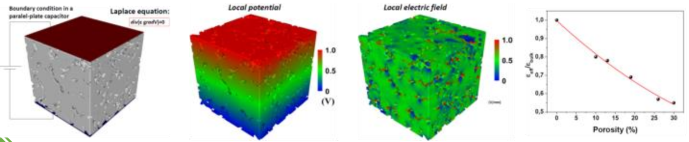


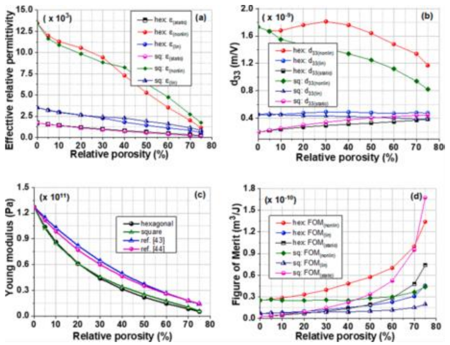


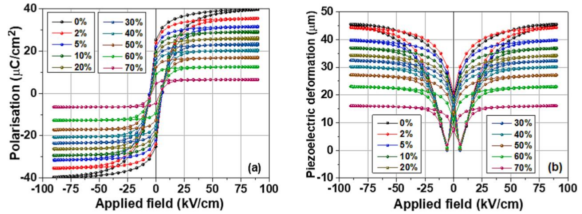




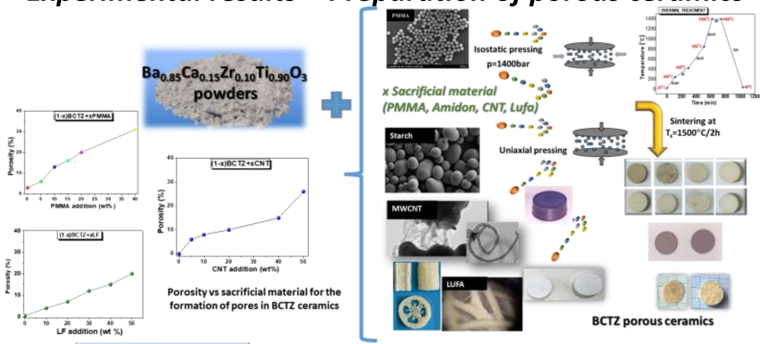
- *Theoretical results - Design of ceramic microstructures and estimation of functional properties using finite element models (FEM)*



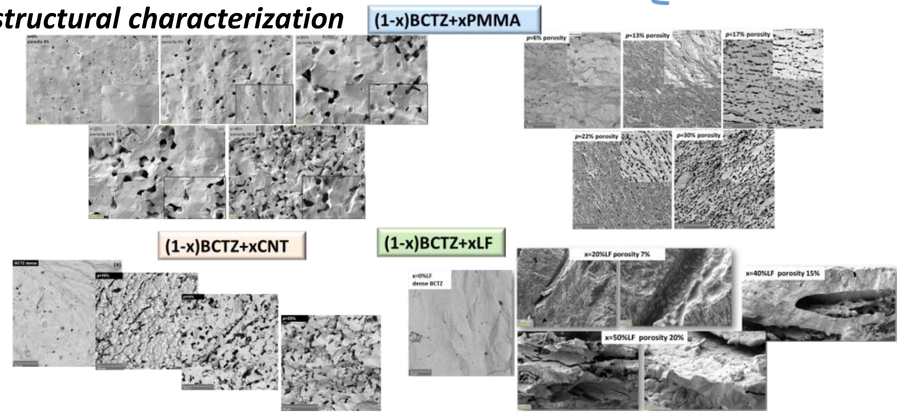




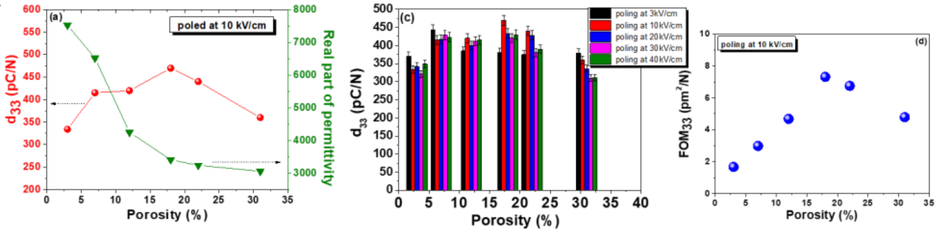
- *Experimental results – Preparation of porous ceramics*



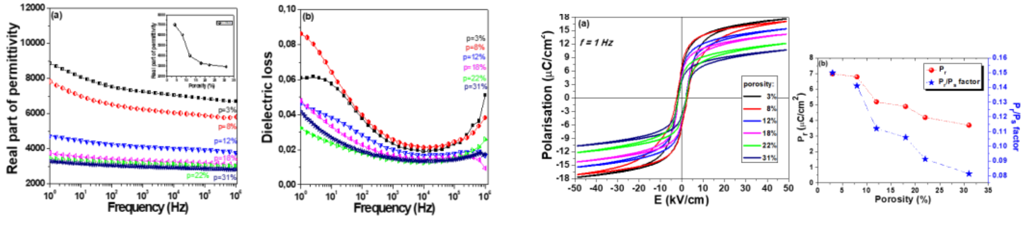
- *Experimental results – microstructural characterization*



- *Experimental results – FOM piezoelectric response*



- *Experimental results - electrical properties*



O1

O1. Material design using theoretical models (FEM combined with Landau-Ginzburg-Devonshire theory).

Prime novelty at national and international level:

(i) understanding the relationship between pore geometry and polarization behavoiur in porous ferroelectric materials, its impact on piezo/pyroelectric properties;

(ii) simulations of porous microstructures with the best piezo and pyroelectric properties and improved FOM.

O2

O2. Development of Pb-free porous ceramics with improved piezo-/pyroelectric FOMs

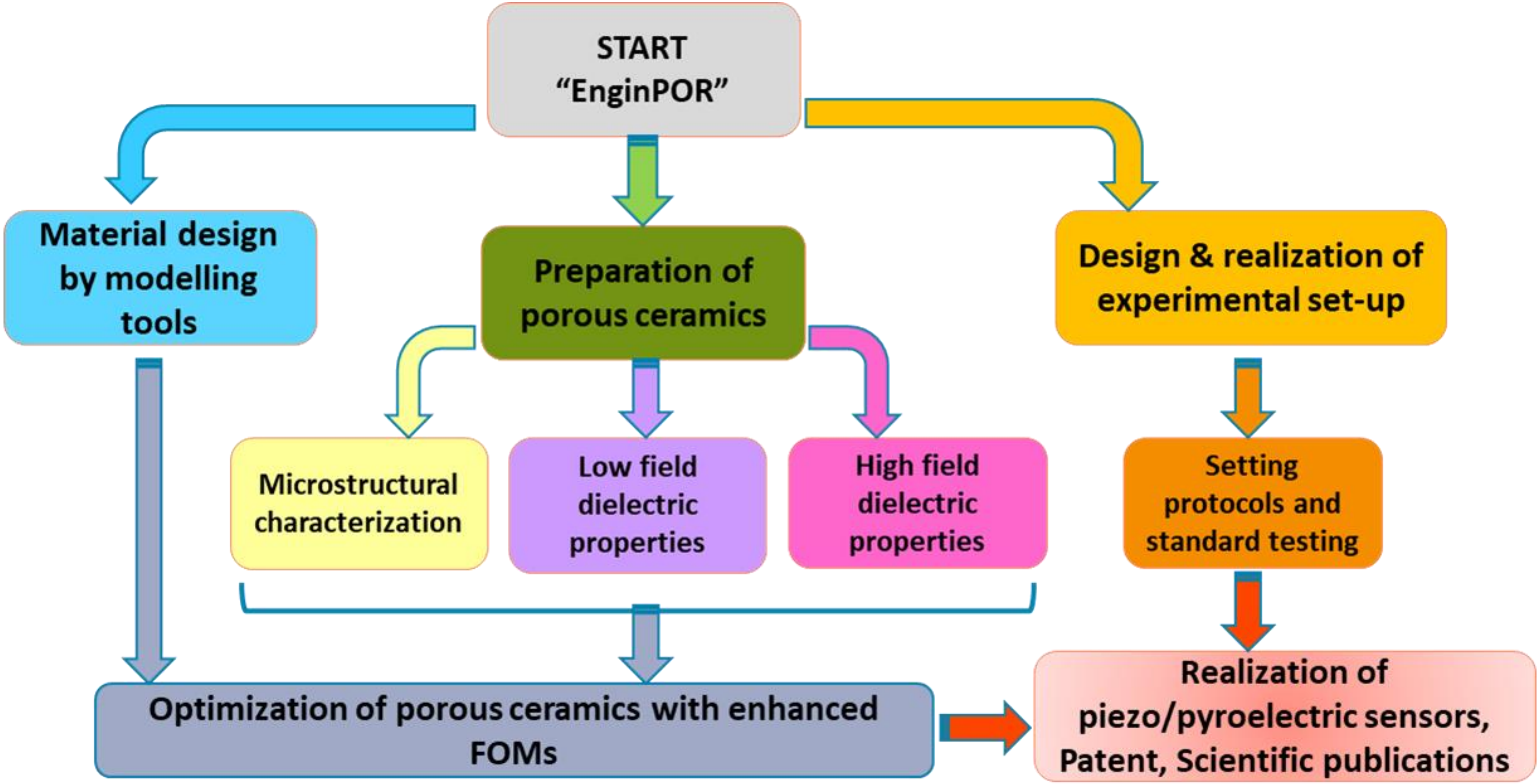
1. Preparation, optimization and microstructural characterization of Pb-free porous ceramics;
2. Functional characterization of Pb-free porous ceramics (dielectric, ferro-, piezo-pyroelectric and nonlinear properties).

O3

O3. Design of experimental devices for testing the produced and optimized porous ceramics (piezo- and pyroelectric sensors)

Design of experimental devices for testing of produced and optimized porous ceramics (piezo- and pyroelectric sensors)

Project methodology



O1

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(i) understanding the relationship between pore geometry and polarization behavoiur in porous ferroelectric materials, its impact on piezo/pyroelectric properties;

(ii) simulations of porous microstructures with the best piezo and pyroelectric properties and improved FOM.

A1.1 Developing of combined models for simulating the porous microstructures and estimation of piezoelectric response in porous materials (2021 activity).

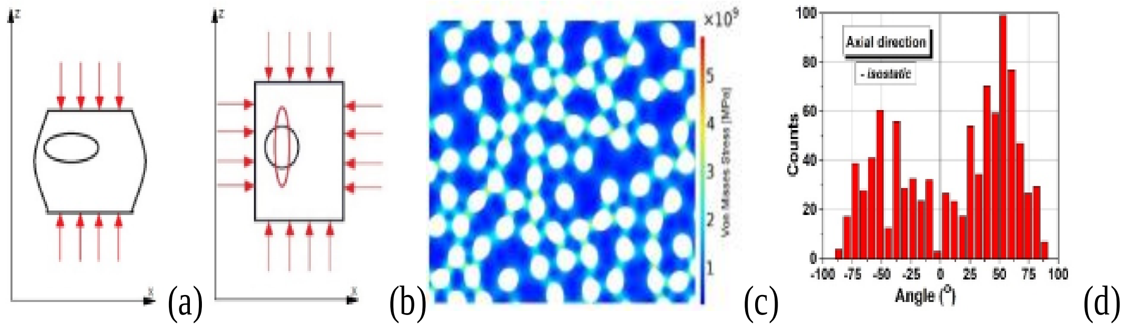
A1.2-A2.1-A3.1 Study of the impact of electric field distribution on dielectric, piezo/pyroelectric response, P(E) and tunability for different pore shapes (activities in 2021-2022-2023).

A1.3-A2.2-A3.2 Design of piezo-/piezoelectric ceramic microstructures, using theoretical models, with improved FOM (activities in 2021-2022-2023).

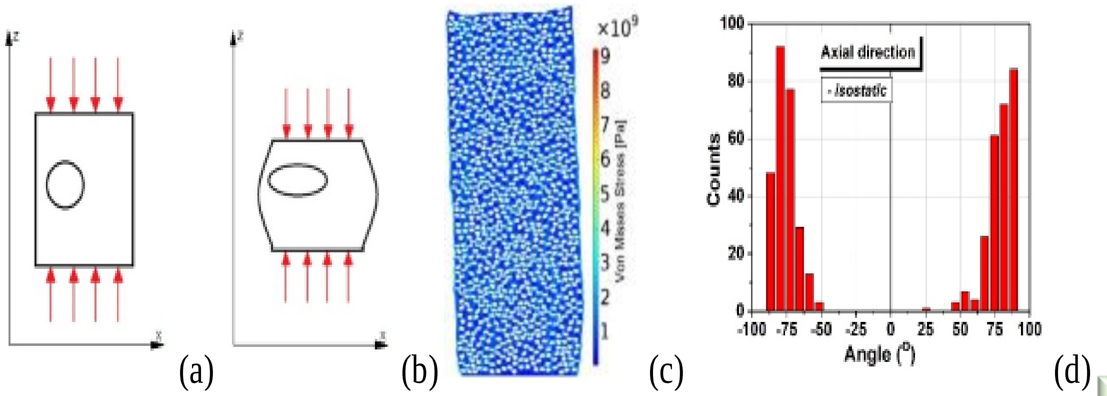
Act 2.3-A3.3 Theoretical validation of functional properties (dielectric, ferroelectric and piezo/pyroelectric properties) for real microstructures (activities in 2022-2023).

O1. Material design using theoretical models

- **A 2D numerical model in longitudinal and transverse section relative to the axis of a cylinder, based on finite element calculations (FEM) using the COMSOL Multiphysics package, was built to simulate the behavior of the sample with spherical inclusions during compression in transverse and longitudinal section.**

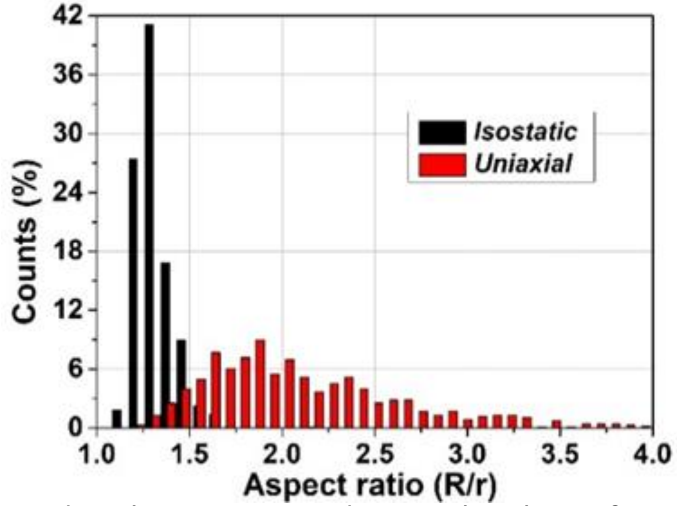


Schematic of isostatic pressing: (a) pressure applied only along the cylinder axis, (b) after isostatic pressing and deformation; (c) isostatically deformed structure; (d) angular distribution of inclusions derived for the case of isostatic pressing.



Schematic of uniaxial pressing: (**a**) before pressing, (**b**) after pressing and deformation; (**c**) uniaxially entirely deformed structure; (**d**) angular distribution of inclusions derived for uniaxialpressing.

✓ The numerical calculations performed indicated that both modes of pressing lead to the appearance of an anisotropic deformation of the soft inclusions (initially considered circular in the 2D model).

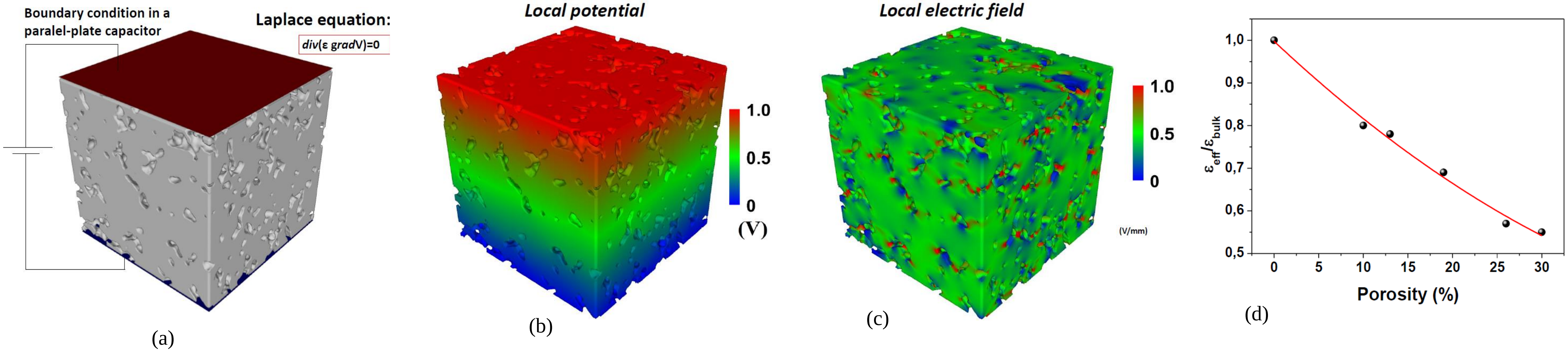


Comparative distributions according to the shape factor R/r resulting from simulations in the case of the two types of pressing (isostatic and uniaxial).

- The results of these simulations obtained during the modeling activities were published in the article ***Mesoscale Models for Describing the Formation of Anisotropic Porosity and Strain-Stress Distributions during the Pressing Step in Electroceramics***, R. S. Stirbu, L. Padurariu, F. F. Chamasemani, R. Brunner, and L. Mitoseriu, Materials 2022, 15, 6839 (ISI=3.4, Q2);

O1. Material design using theoretical models

- **The study of the impact of the electric field distribution on the dielectric response in microstructures with different degrees of porosity** was carried out by developing a **3D finite element model (FEM) to estimate the porosity dependence of the permittivity in ferroelectric ceramics**.



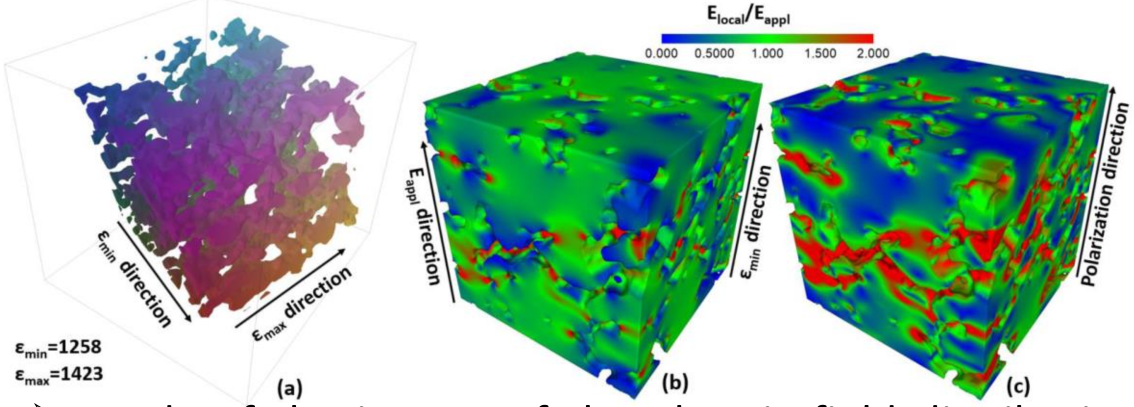
(a) Microstructure with 10% porosity considered in simulations, with boundary conditions; (b),(c) Potential and local field plotted in color scale; (d) Porosity dependence of effective permittivity

- ✓ **Simulations of realistic microstructures showed that a relative ceramic porosity of 10% leads to a decrease in permittivity compared to that of dense ceramics to 80%, and for a relative porosity of 30%, the decrease in permittivity reaches 55% compared to the corresponding one dense material.**

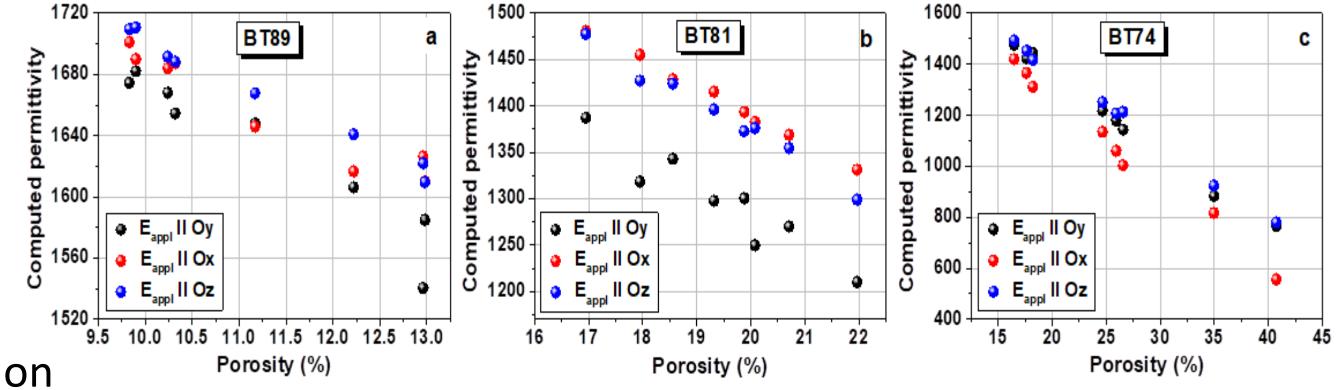
- The results of theoretical simulations and their validation, their comparison with experimental data obtained for the $BaTiO_3$ ferroelectric system were published in the article ***Modifications of structural, dielectric and ferroelectric properties induced by porosity in $BaTiO_3$ ceramics with phase coexistence***, L. Padurariu, L.-P. Curecheriu, C.-E. Ciomaga, M. Airimioaei, N. Horchidan, C. Cioclea, V.-A. Lukacs, R.-S. Stirbu, L. Mitoseriu, Journal of Alloys and Compounds 889, 161699 (2021) (ISI=5.316, Q1)

O1. Material design using theoretical models

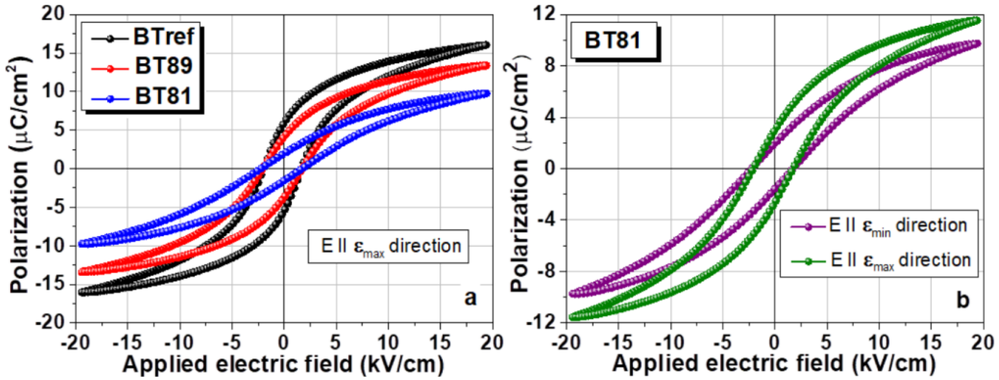
- Specific numerical procedures were performed to reconstruct realistic high-resolution microstructures → 3D microstructures used as input in 3D – FEM to determine the field distributions and local electric potential in the ceramic samples and to evaluate the effective dielectric permittivity and high-field properties as a function of porosity and direction of field application.



FEM-calculated effective permittivities as a function of porosity



- study of the impact of the electric field distribution on the ferroelectric response, P(E), based on the generated 3D microstructures, using the Preisach model and FEM

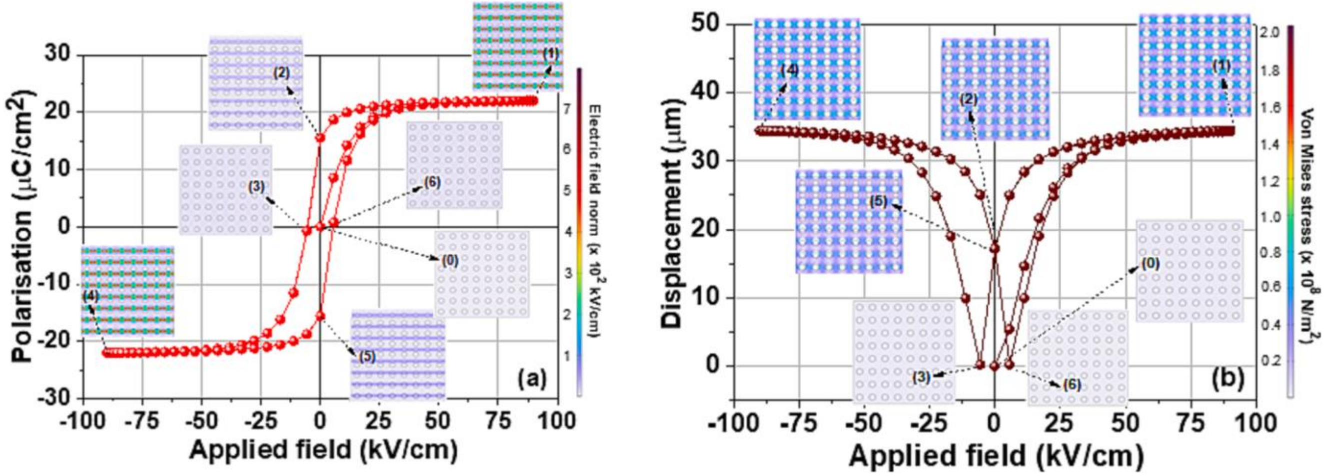


It has been demonstrated the usefulness of analyses and FEM simulations of properties at different length scales, in porous ceramic systems, in completing the understanding of the complex relationship between composition – microstructure – local/macroscopic properties.

- The results of the theoretical simulations and their validation were published in the article ***Analysis of local vs. macroscopic properties of porous $BaTiO_3$ ceramics based on 3D reconstructed ceramic microstructures***, L. Padurariu, F. F. Chamasemani, R. Brunner, L. P. Curecheriu, V. A. Lukacs, R. S. Stirbu, C. E. Ciomaga, L. Mitoseriu, Acta Materialia 255 (2023) 119084 (ISI=9,4 Q1)

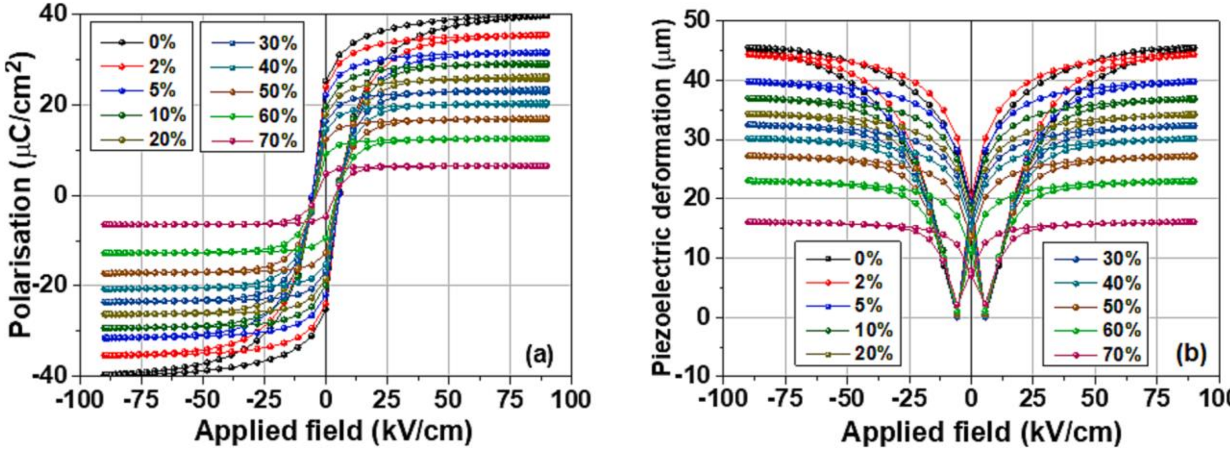
O1. Material design using theoretical models

➢ **The evolution of the polarization, stresses and piezoelectric response created by applying different electric field values was modeled using the Jiles-Atherton model combined with finite element analysis (FEM)**



✓ polarization *vs.* electric field, and mechanical deformations vs. field give a realistic description of the influence of porosity on hysteresis cycles, and these results could be observed and compared with experimental data for different ferroelectric systems that present variable porosities.

(a) P(E) simulations for different electric field distributions; and (b) piezoelectric displacement vs. electric field s(E) for a relative value of 18% porosity and Von Mises stress distribution in different states: (0) depolarized state; (1) at positive saturation bias; (3) at negative coercive field; (4) at negative saturation bias; (5) at negative remanent bias; (6) at positive coercive field.

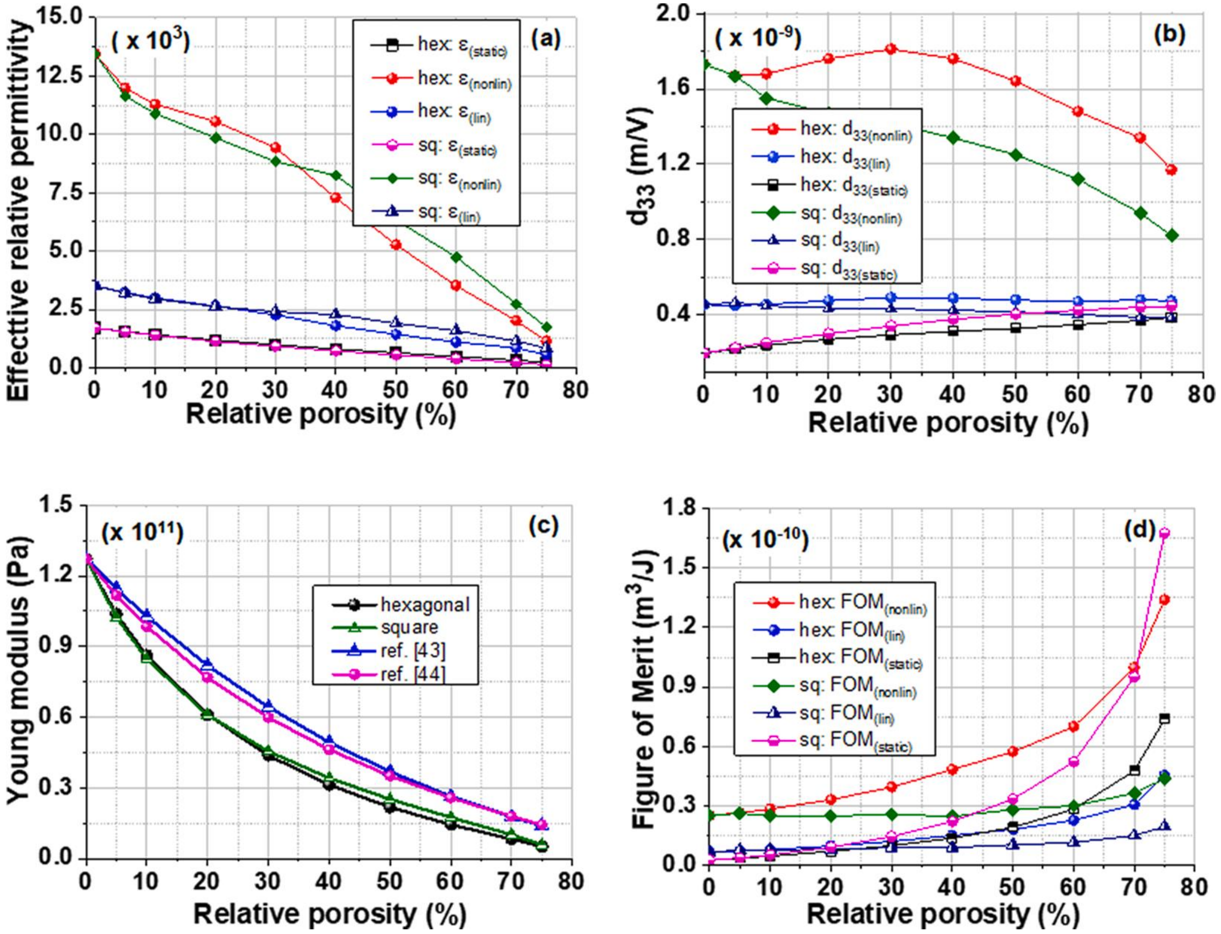


✓ In a ferroelectric structure, a porosity increase leads to a non-linear decrease in the average ferroelectric polarization and the strain/piezoelectric response, as a result of the inhomogeneity of the electric field and the Von Mises stress as well as the reduction of the amount of piezoelectric phase

FEM simulation and calculation based on the Jiles-Atherton model of polarization hysteresis and piezoelectric deformations by applied electric field in a ferroelectric system with a uniformly distributed porosity.

O1. Material design using theoretical models

➢ **Using the FEM, the simulation of porous piezoelectric/pyroelectric ceramic structures was carried out to study the influence of porosity on the effective permittivity, the piezoelectric coefficient d_{33}, Young's modulus Y and the figure of merit (FOM) of the piezoelectric response.**



(a) Effective permittivity, (b) piezoelectric coefficient d33, (c) Young's modulus, and (d) FOM vs. the relative porosity in static and remanence conditions, at the increase and decrease of the applied electric field.

✓ The simulation results showed a decrease in dielectric permittivity and Young's modulus with increasing porosity. Theoretical estimates have shown that there is an optimum porosity (10-20% porosity) for which the porous microstructures show an increase in the piezoelectric coefficient (d_{33}) and an improvement in the FOM.

• The results of the theoretical studies and their validation using experimental data were achieved by publication in the paper ***Modeling of hysteretic response of porous piezo/ferroelectric ceramics***, R. S. Stirbu and L. Mitoseriu, Computational Materials Science (2023) (ISI=3.3 Q2)

Deliverables achieved through theoretical modeling activities A1.1, A1.2-A2.1-A3.1, A1.3-A2.2-A3.2 , A2.3-A3.3 :

(i) it was demonstrated by analytical and numerical calculation that by both uniaxial and isostatic pressing the spherical inclusions deform and they will generate anisotropic porosity in the porous ceramic after sintering;
(ii) the mechanical strain-stress dependencies were studied and the differences between the microstructures of the porous ceramics obtained by two types of uniaxial and isostatic pressing were shown and discussed;
(iii) from simulations and theoretical calculation, it was shown that there is an optimum porosity ~ 10-20% for which the piezoelectric response increases, unlike dense ceramics;
(iv) porous microstructures with different pore shapes were designed using both analytical and FEM models;
(v) the calculation and simulation of the electric field distributions and the dielectric response for different porous microstructures was performed, and these were validated by comparing them with experimental results obtained on porous $BaTiO_3$ ceramics;
(vi) program codes were written to calculate by FEM finite element method the dependence of effective permittivity, polarization, pyroelectric response, nonlinear properties and elastic properties in ferroelectric structures with different degrees of porosity and for different pore geometries .

Deliverables 4 ISI articles:

1. ***Modifications of structural, dielectric and ferroelectric properties induced by porosity in $BaTiO_3$ ceramics with phase coexistence***, L. Padurariu, L.-P. Curecheriu, C.-E. Ciomaga, M. Airimioaei, N. Horchidan, C. Cioclea, V.-A. Lukacs, R.-S. Stirbu, L. Mitoseriu, Journal of Alloys and Compounds 889, 161699 (2021) (ISI=5.316, Q1)
2. ***Mesoscale Models for Describing the Formation of Anisotropic Porosity and Strain-Stress Distributions during the Pressing Step in Electroceramics***, R. S. Stirbu, L. Padurariu, F. F. Chamasemani, R. Brunner, and L. Mitoseriu, Materials 2022, 15, 6839 (ISI=3.4, Q2)
3. ***Analysis of local vs. macroscopic properties of porous $BaTiO_3$ ceramics based on 3D reconstructed ceramic microstructures***, L. Padurariu, F. F. Chamasemani, R. Brunner, L. P. Curecheriu, V. A. Lukacs, R. S. Stirbu, C. E. Ciomaga, L. Mitoseriu, Acta Materialia 255 (2023) 119084 (ISI=9,4 Q1)
4. ***Modeling of hysteretic response of porous piezo/ferroelectric ceramics***, R. S. Stirbu and L. Mitoseriu, Computational Materials Science (2023) (ISI=3.3 Q2)

O1. Material design using theoretical models

O2. Development of Pb-free porous ceramics with improved piezo-/pyroelectric FOMs

A1.4 Synthesis and microstructural characterization of powders based on solid solutions of BT doped in A and/or B positions of the perovskite cell for their use as a ferroelectric matrix (activity in 2021).

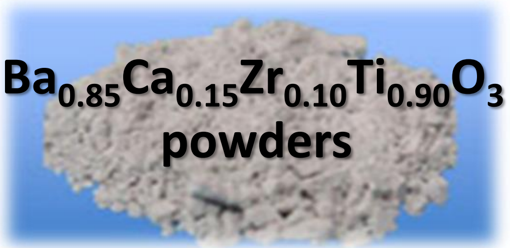
A1.5 - A2.4 - A3.4 Production of Pb-free porous ceramics (with different types of pore connectivity) (activities in 2021-2022-2023).

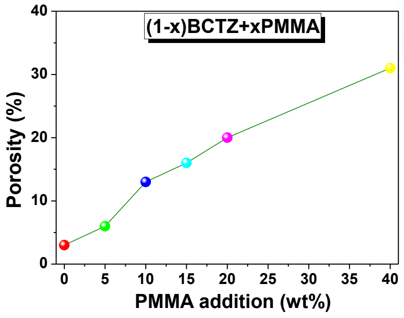
Act 2.5 - Microstructural characterization of Pb-free porous ceramics; selection of structures with superior piezo-/pyroelectric response for FOM improvement (activity in 2022).

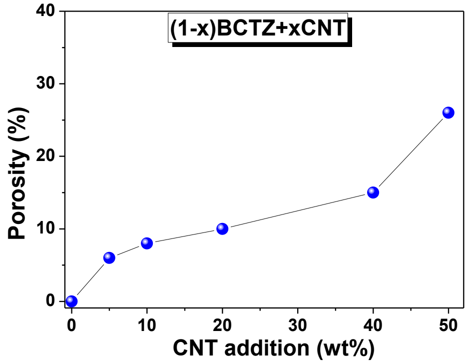
Act 2.6 – A3.5 Study of the effect of porosity on dielectric properties at low and high electric fields (activity in 2022-2023).

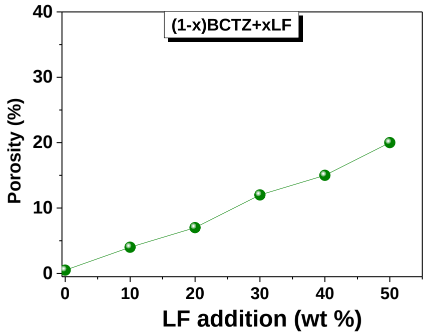
O2. Production of Pb-free porous ceramics (with different types of pore connectivity)

- It has been produced $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ ceramics with different degrees of porosity using different sacrificial materials and different pressing techniques:

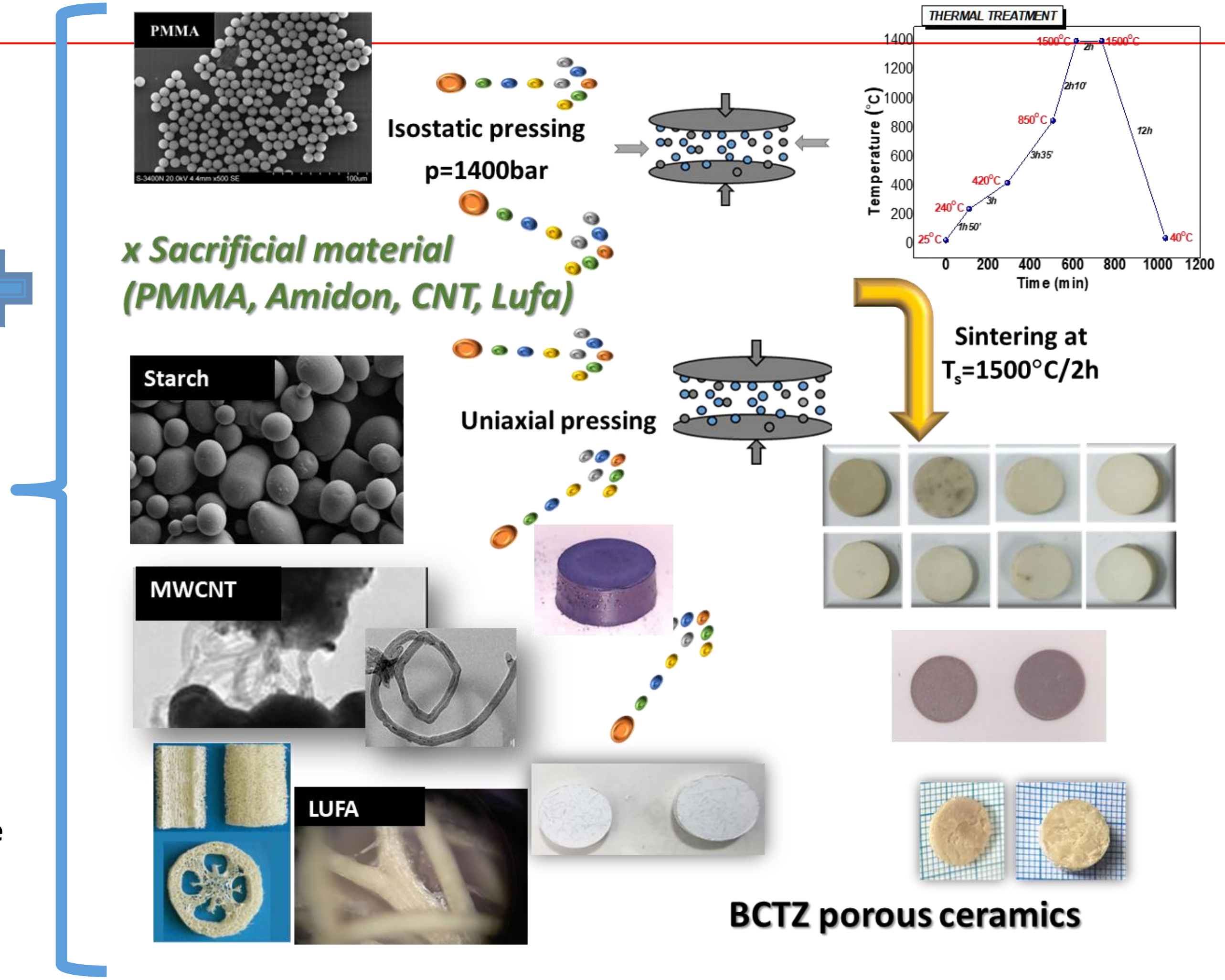








Porosity vs sacrificial material for the formation of pores in BCTZ ceramics

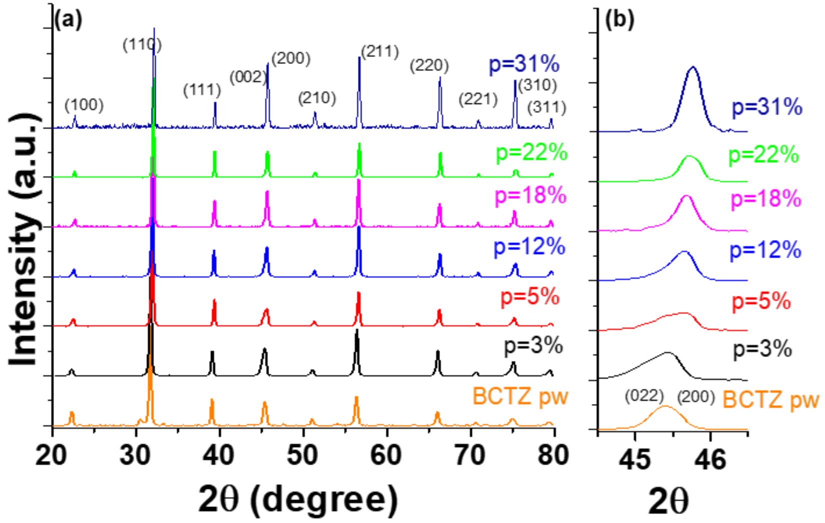


- The results of these syntheses, optimization and the functional properties of the produced ceramics were published in a scientific paper ***Optimization of processing steps for superior functional properties of (Ba, Ca)(Zr, Ti)O3 ceramics***, C. E. Ciomaga, L. P. Curecheriu, V. A. Lukacs, N. Horchidan, F. Doroftei, R. Valois, M. Lheureux, M. H.e Chambrier and L. Mitoseriu, Materials 2022 15 (24), 8809 (ISI=3.4, Q2);

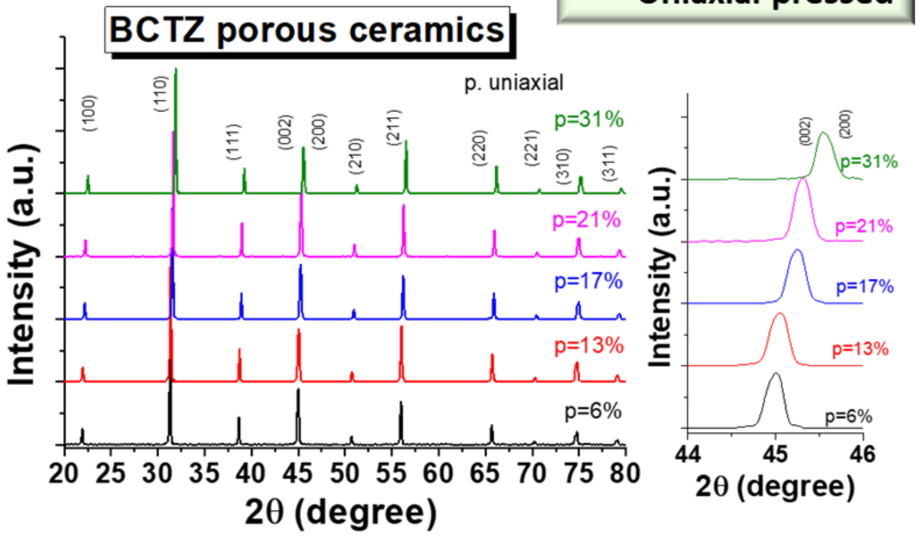
• Structural analysis by X-ray diffraction (XRD)

(1-x)BCTZ+xPMMA

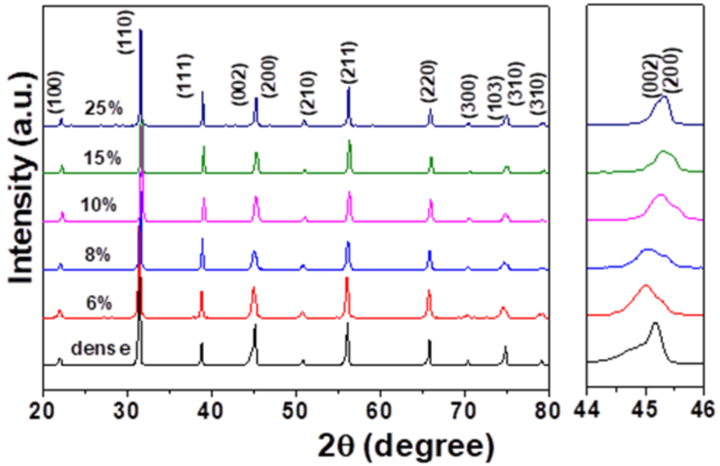
• Isostatic pressed



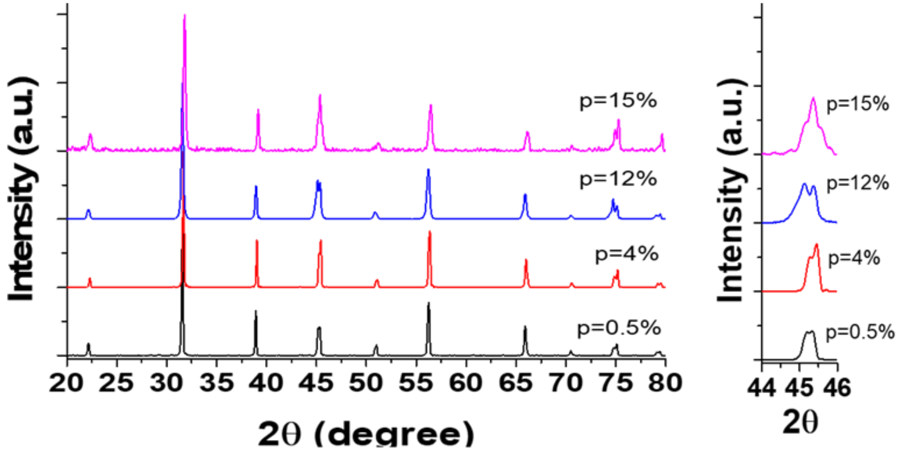
• Uniaxial pressed



(1-x)BCTZ+xCNT



(1-x)BCTZ+xLF



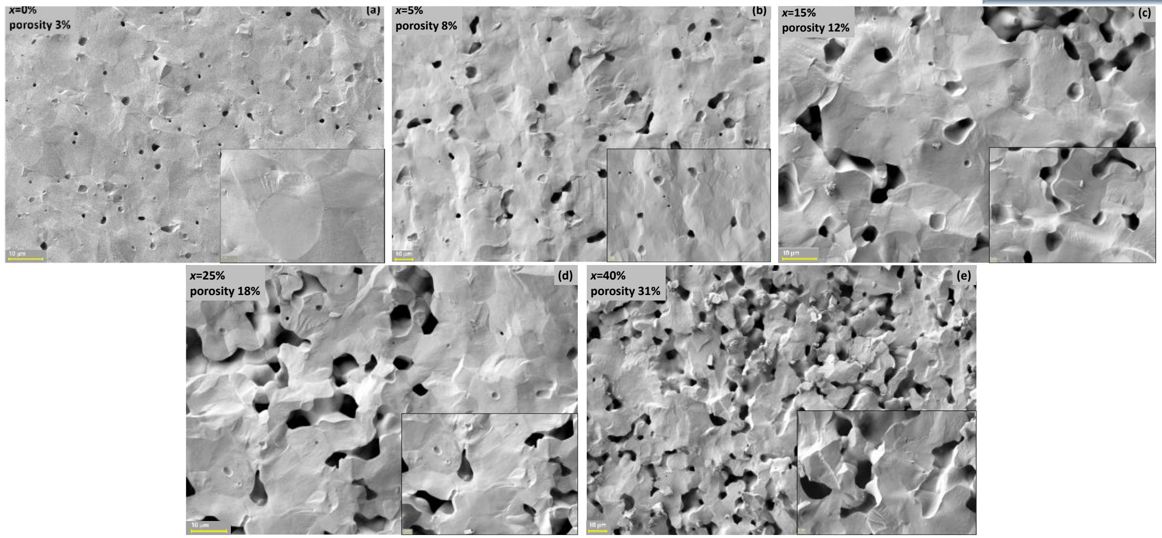
✓ porous BCTZ ceramics with composition at MPB presents a superposition/mixture of phases

• Microstructural characterization of Pb-free porous ceramics (SEM)

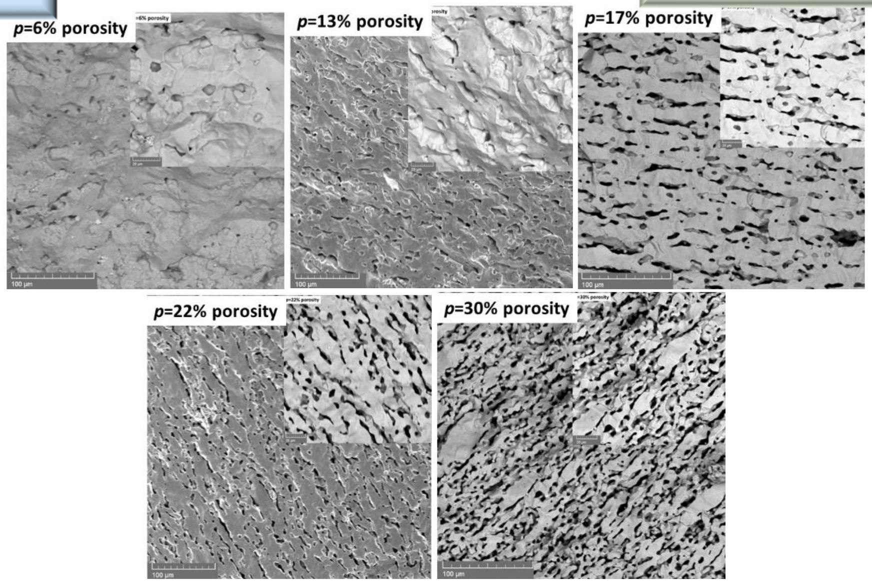
➢ The increasing porosity level leads to a strong impact on the ceramic morphology ⇒ modification of pore shape, size, and connectivity.

(1-x)BCTZ+xPMMA

• Isostatic pressed

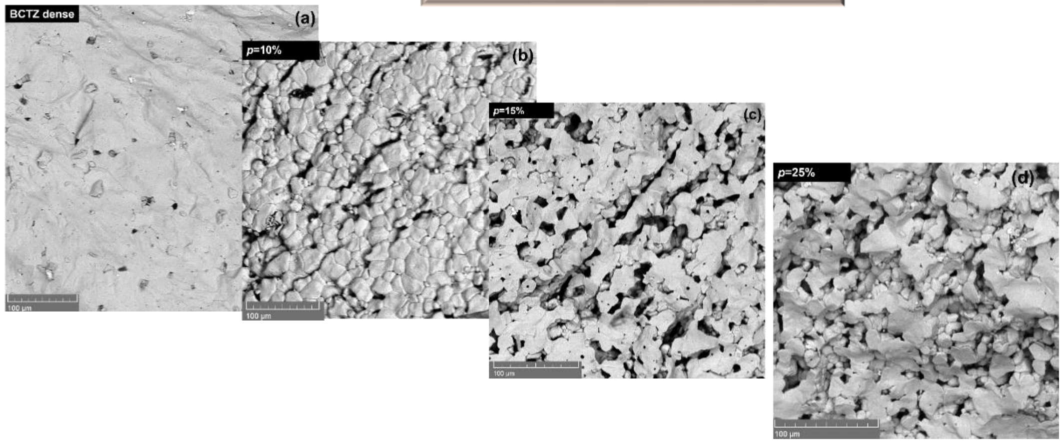


• Uniaxial pressed



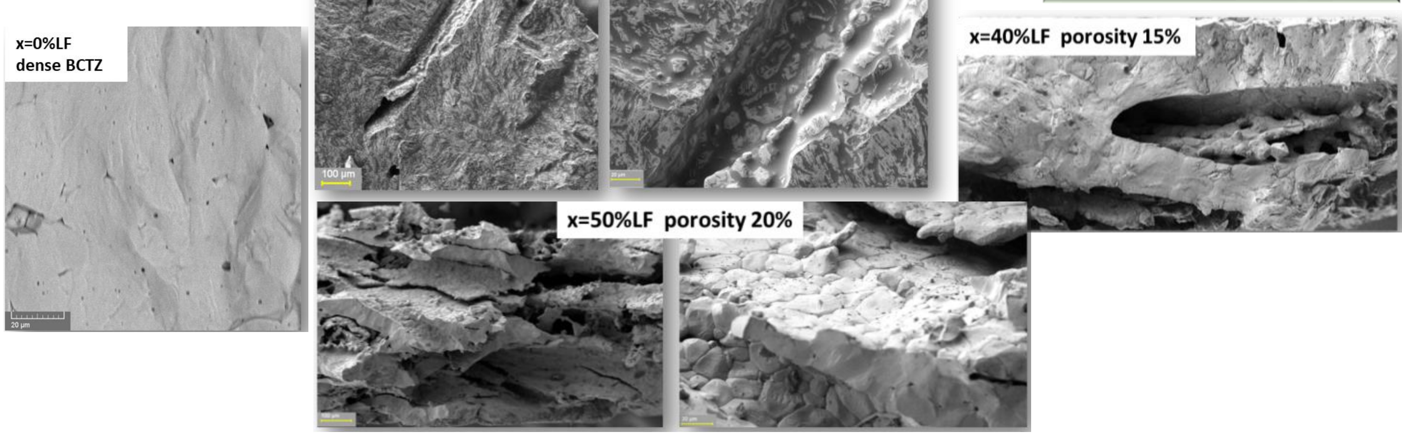
• Uniaxial pressed

(1-x)BCTZ+xCNT



(1-x)BCTZ+xLF

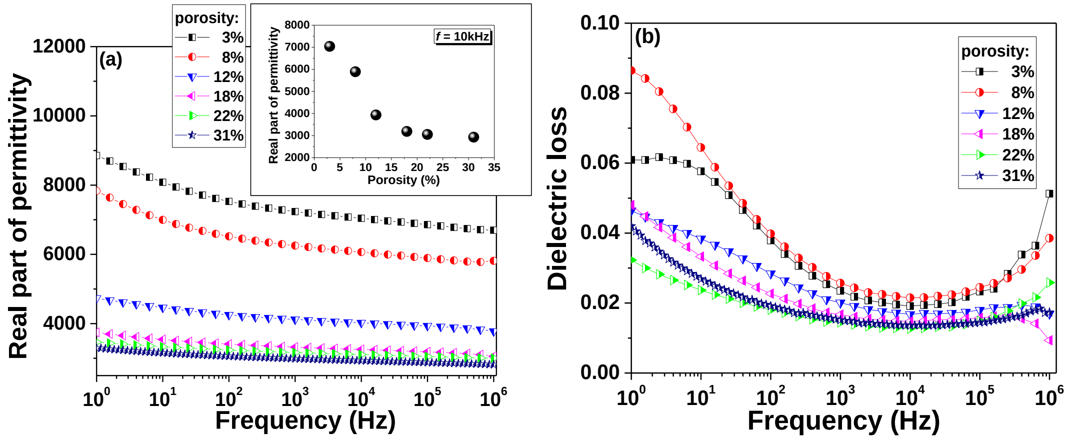
• Uniaxial pressed



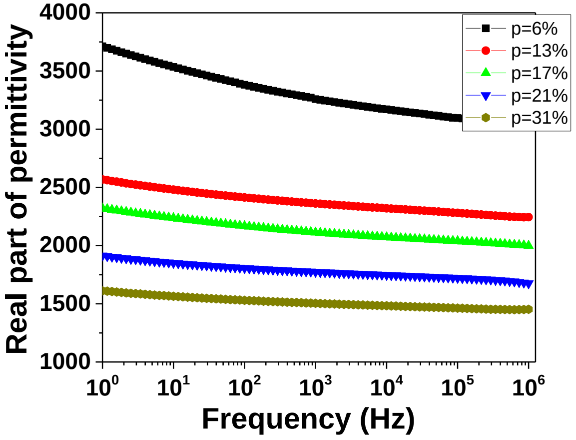
• Dielectric properties at low fields la T_{cam}, f=1Hz-1MHz

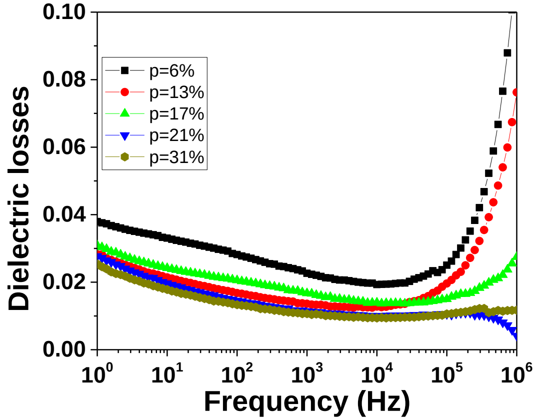
(1-x)BCTZ+xPMMA

• Isostatic pressed



• Uniaxial pressed

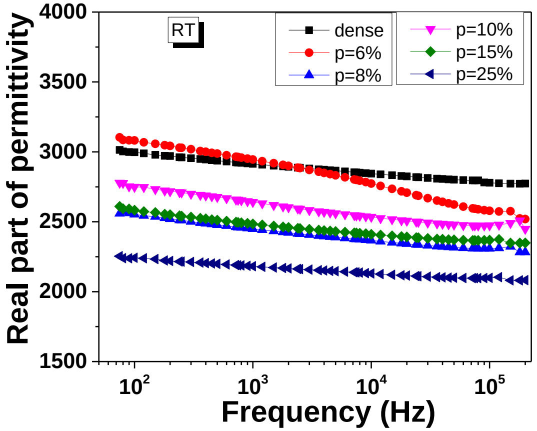


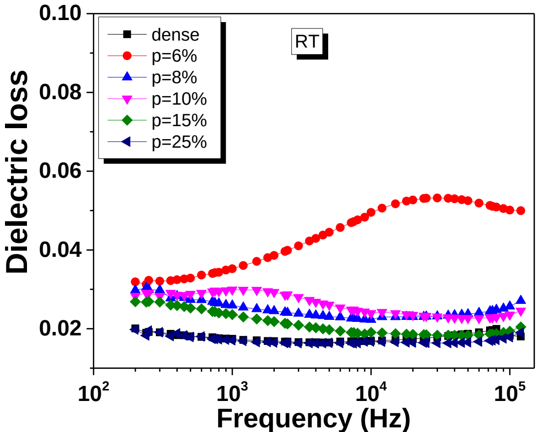


- ➢ gradual reduction of dielectric permittivity with increasing porosity - "dilution effect" ;
- ➢ dielectric loss is below 3% in all frequency ranges, for all the ceramics.

(1-x)BCTZ+xCNT

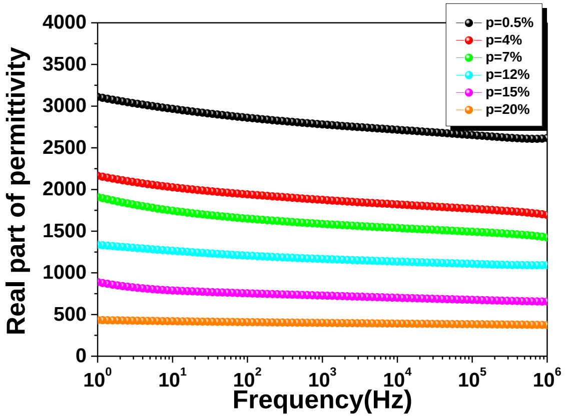
• Uniaxial pressed

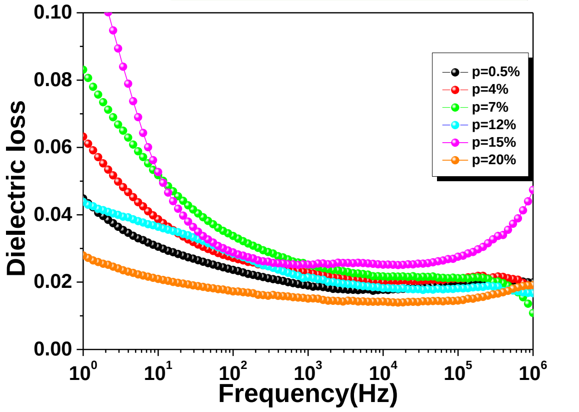




(1-x)BCTZ+xLF

• Uniaxial pressed

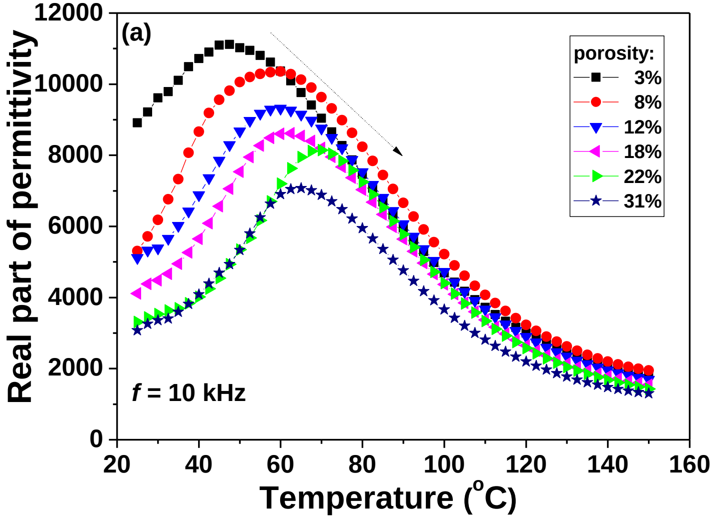




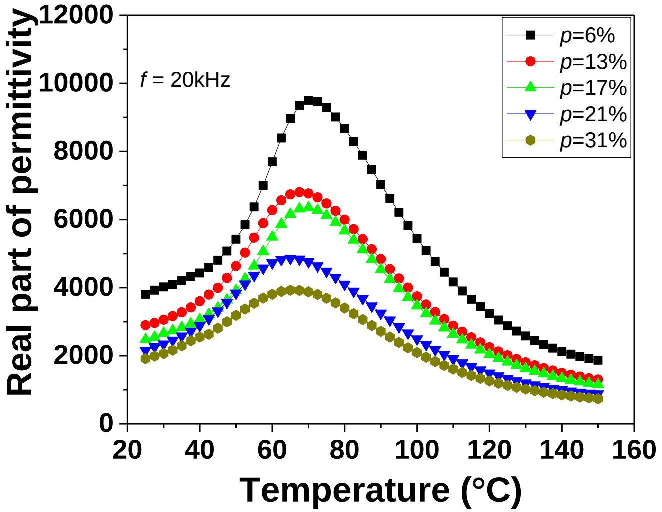
• Dielectric properties at low fields for *T*=20-150°C, at *f*=10kHz

(1-x)BCTZ+xPMMA

• Isostatic pressed

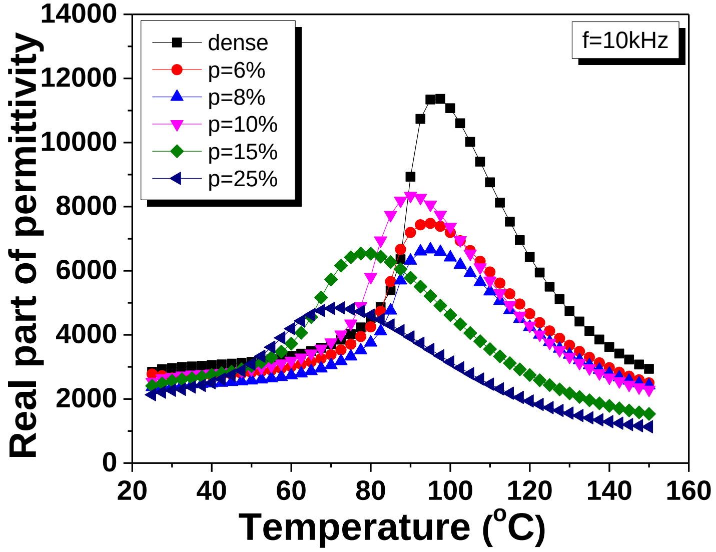


• Uniaxial pressed



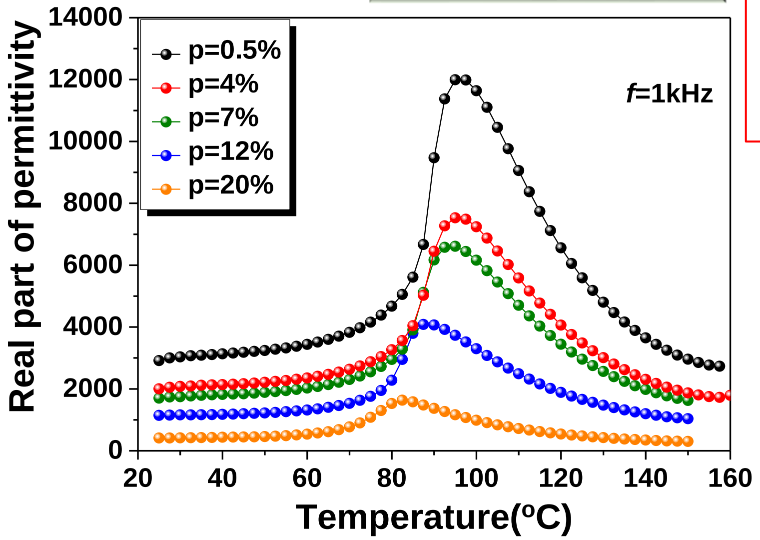
(1-x)BCTZ+xCNT

• Uniaxial pressed



(1-x)BCTZ+xLF

• Uniaxial pressed



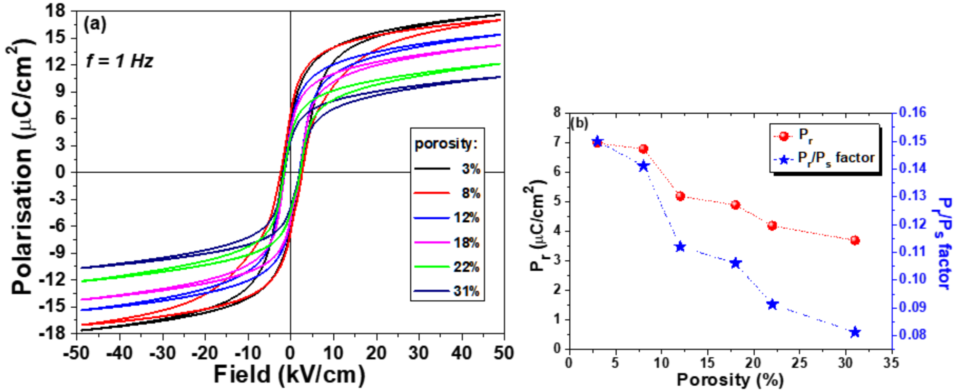
- **when increasing porosity → decrease of ε / T_C shift / broadening of ferro-para phase transition.**

✓ The shift of T_C is explained in terms of the internal stresses that occur through the appearance of porosity in the BCTZ ceramic, as well as possible structural changes due to the order of Ca and Ba cations in the system.

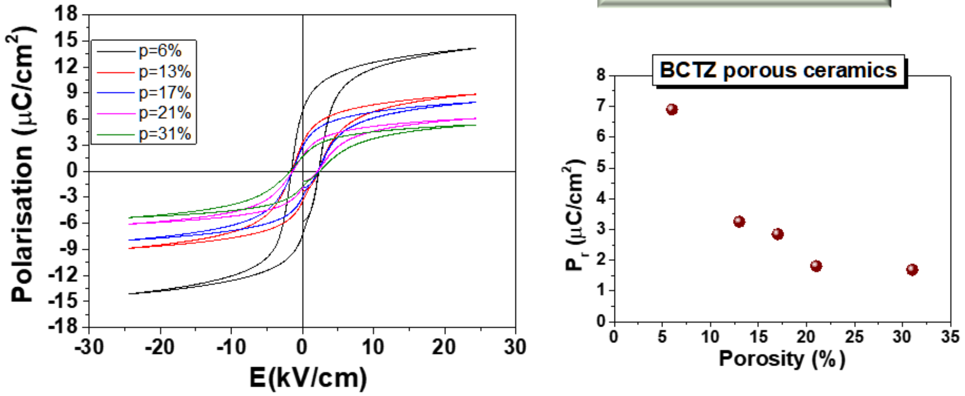
• Ferroelectric properties – effect of porosity on polarization at high fields

(1-x)BCTZ+xPMMA

• Isostatic pressed

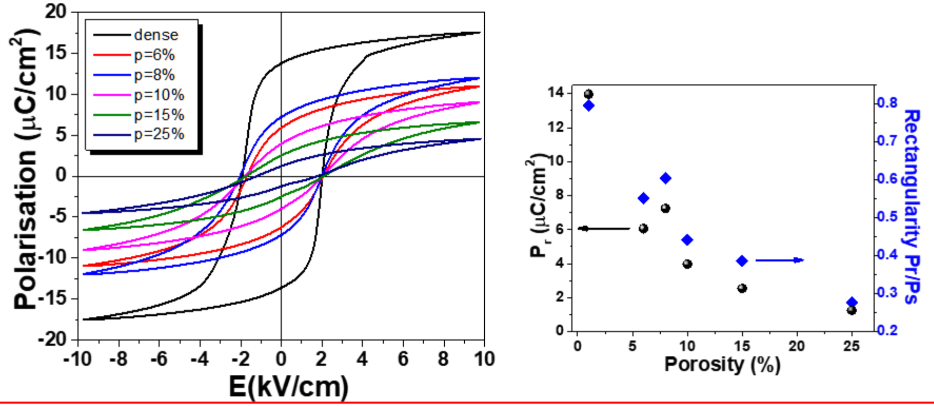


• Uniaxial pressed



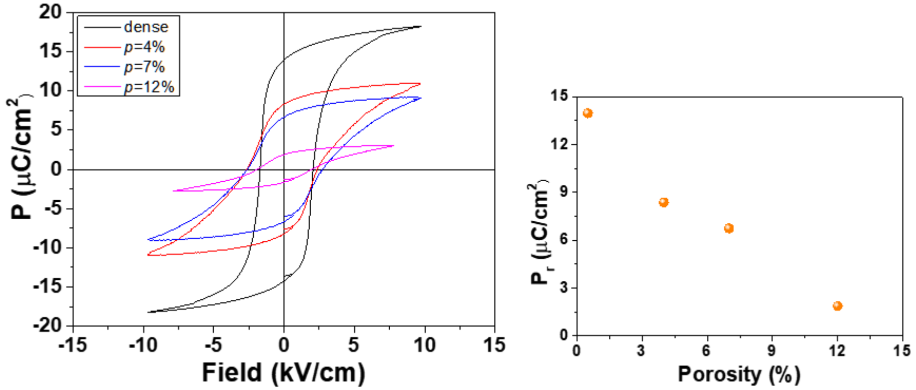
(1-x)BCTZ+xCNT

• Uniaxial pressed



(1-x)BCTZ+xLF

• Uniaxial pressed

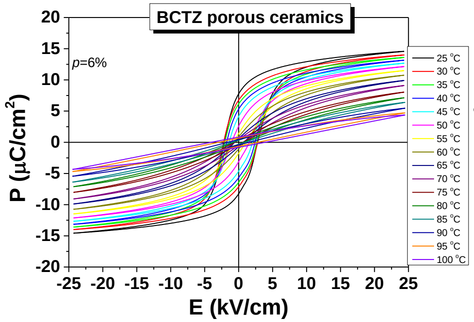


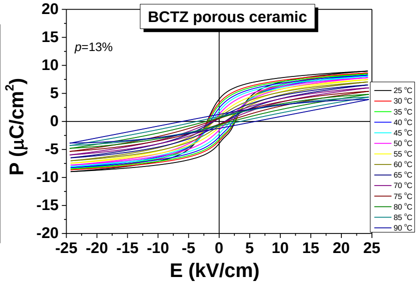
- By increasing porosity a decrease of P_r and a tilting of *P(E)* loops were observed.
- The remnant polarization decreased with an increase in porosity due to the reduced amount of ferroelectric phase and the additional depolarization factor determined by the shape of the pore and the associated electric field distribution around the pore.

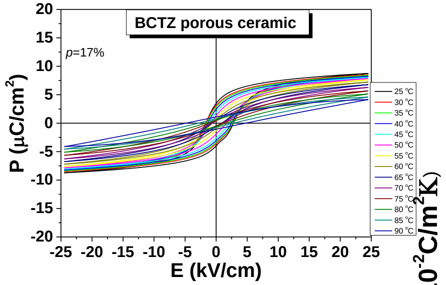
• Ferroelectric properties – pyroelectric response

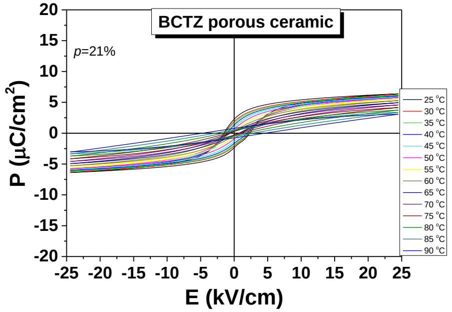
• Uniaxial pressed

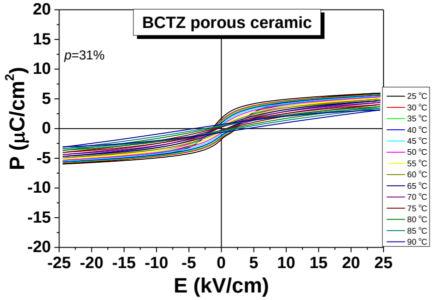
(1-x)BCTZ+xPMMA

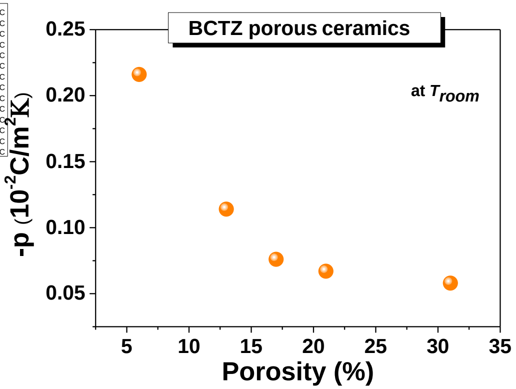






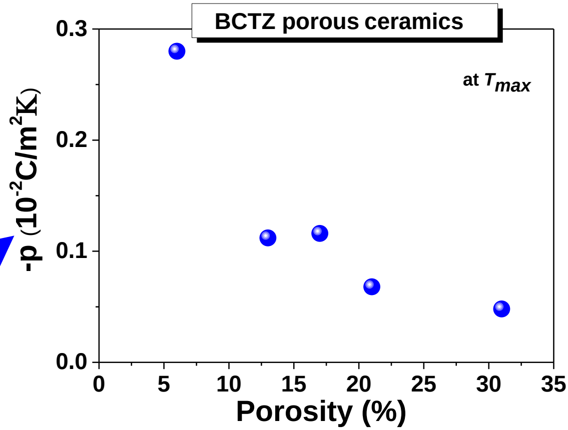


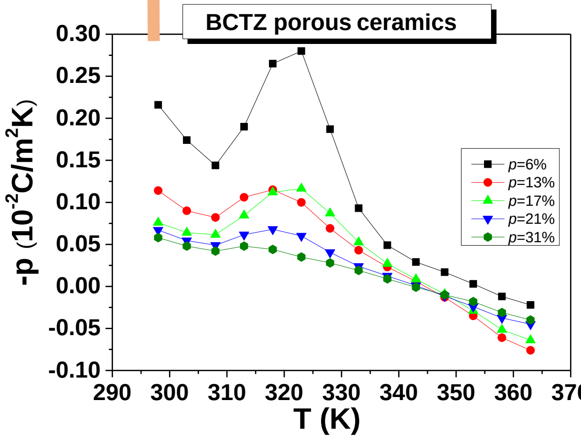




- pyroelectric coefficient

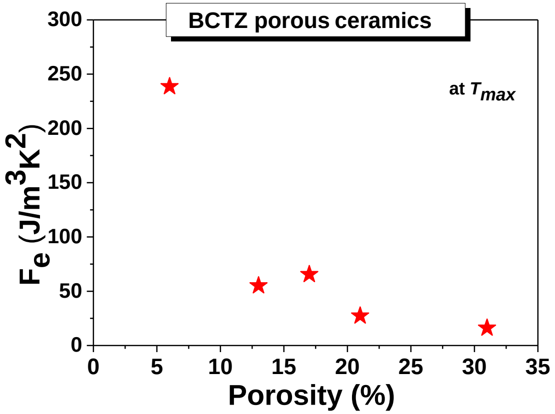
$$p = \frac{\partial P}{\partial t}$$





Pyroelectric energy harvesting FOM (F_e)

$$F_e = p^2 / \varepsilon_0 \varepsilon$$

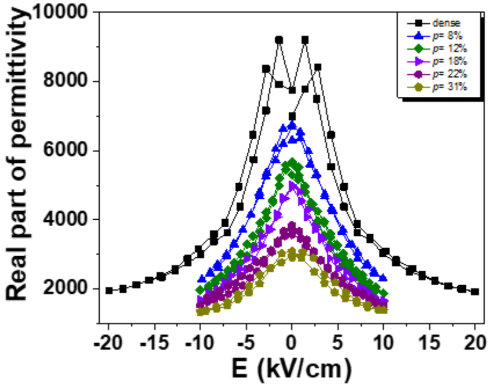


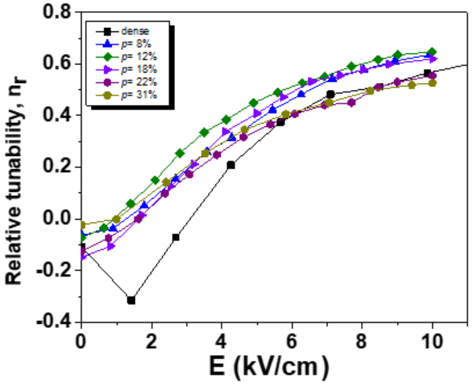
✓ For a temperature of 50°C, the pyroelectric coefficient presents a maximum corresponding to the Curie temperature of the BCTZ system.

• Non-linear properties at high fields dc-tunability

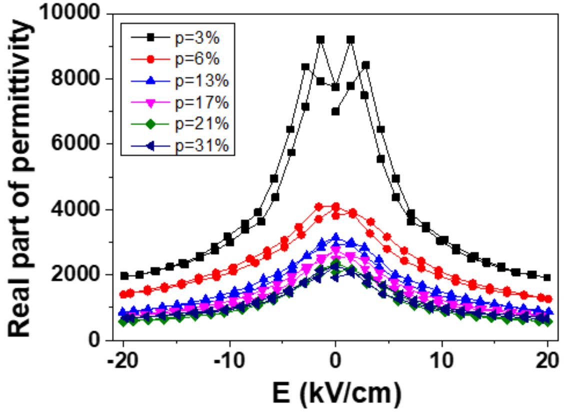
(1-x)BCTZ+xPMMA

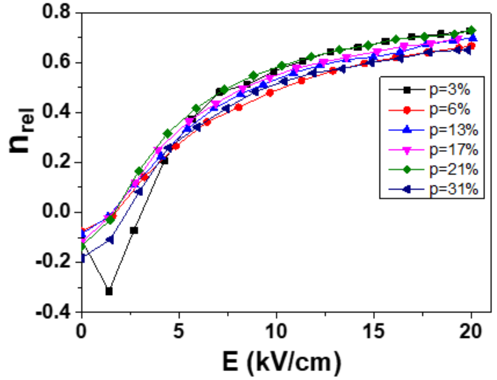
• Isostatic pressed





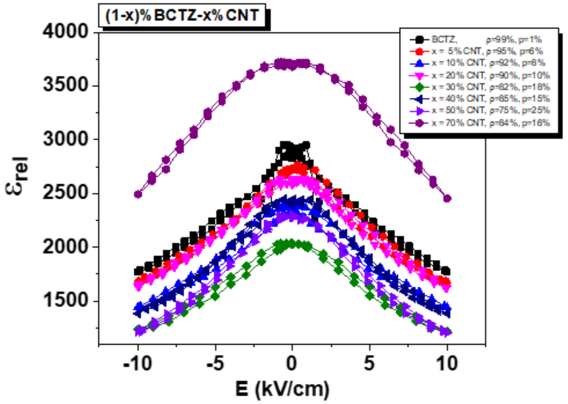
• Uniaxial pressed

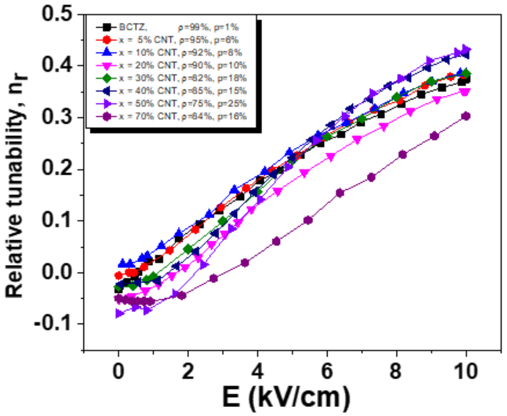




(1-x)BCTZ+xCNT

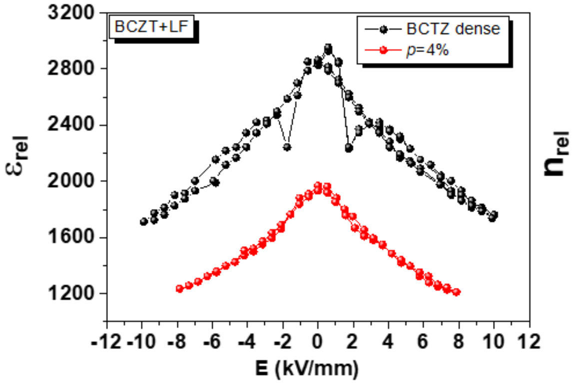
• Uniaxial pressed

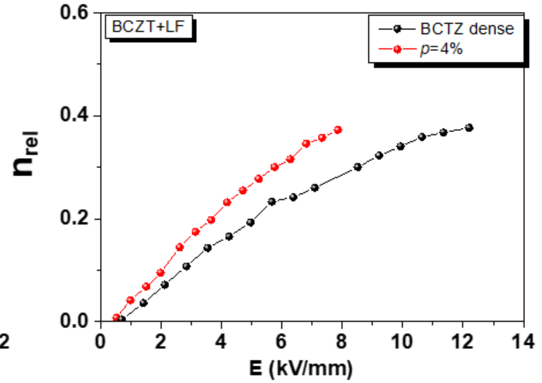




(1-x)BCTZ+xLF

• Uniaxial pressed



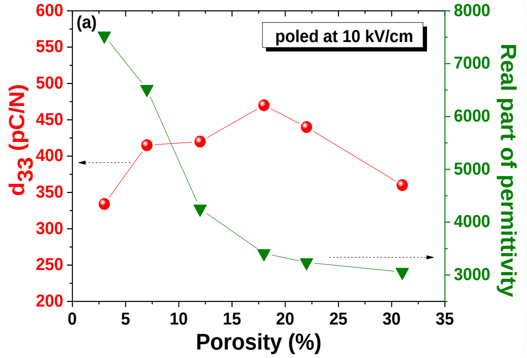


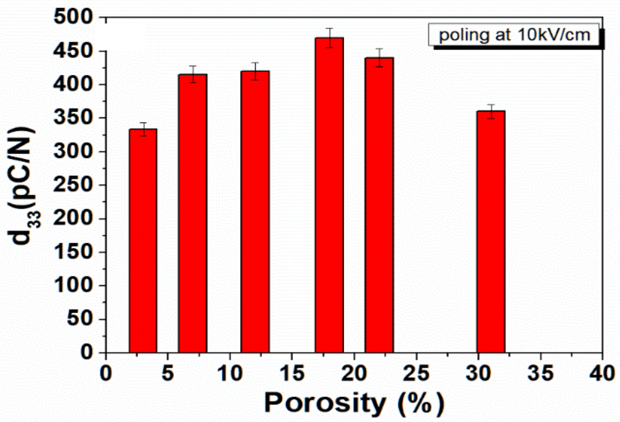
✓ for optimum porosity of 12% → relative tunability higher than in the dense BCTZ ceramic.

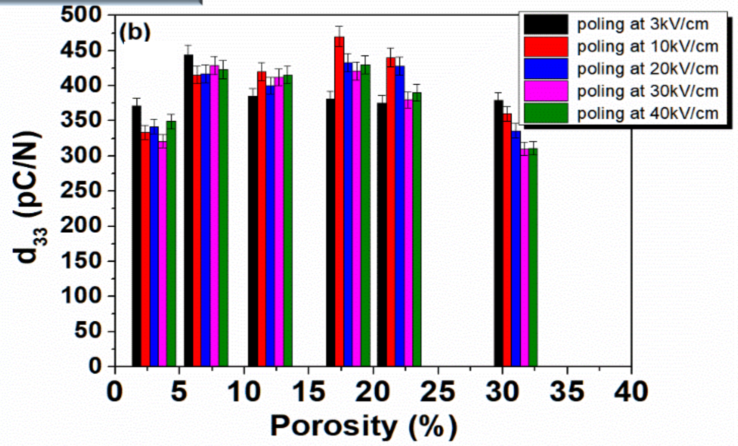
• Piezoelectric coefficient and Figure of Merit (FOM) of piezoelectric response

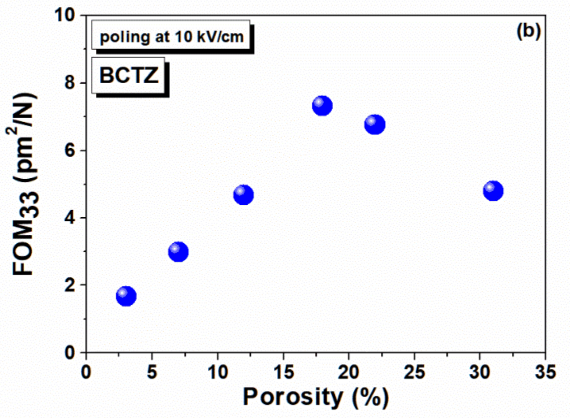
(1-x)BCTZ+xPMMA

- Isostatic pressed



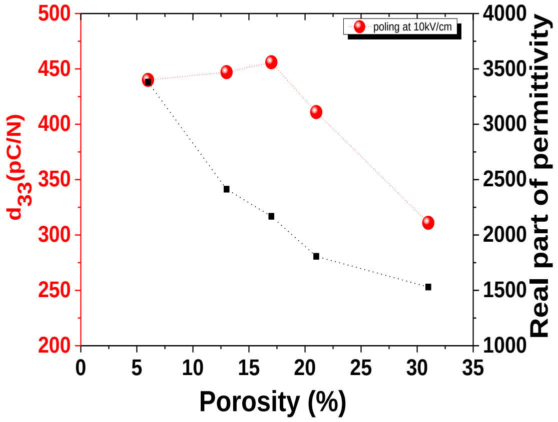


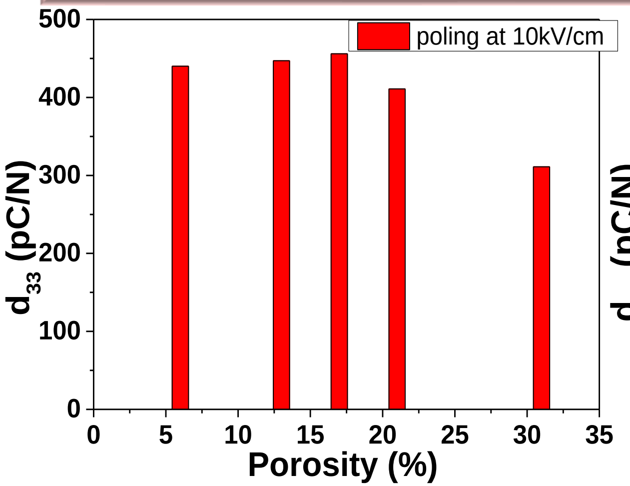


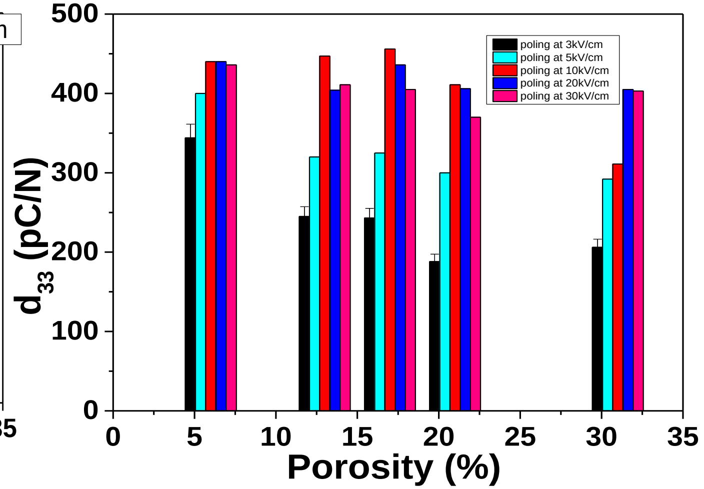


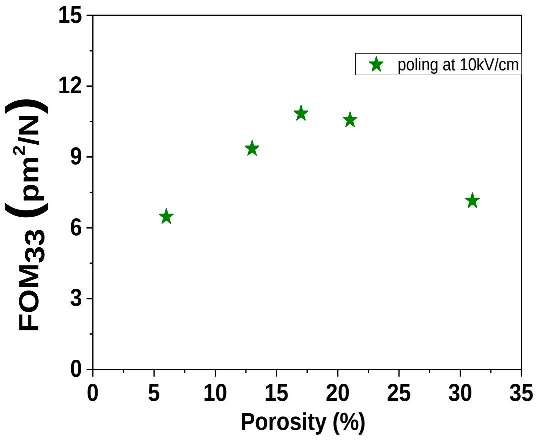
➢ Piezoel. coefficient d_{33} increase, while the permittivity decreases with the increase of porosity – *requirements for materials with enhanced FOM*

- Uniaxial pressed







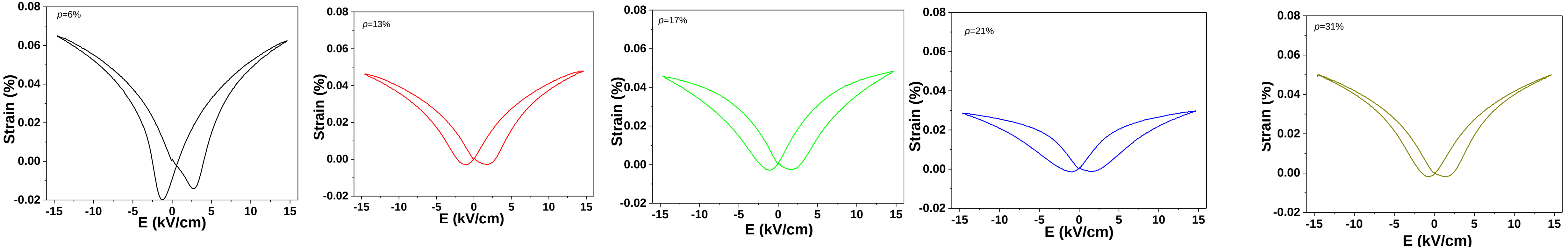


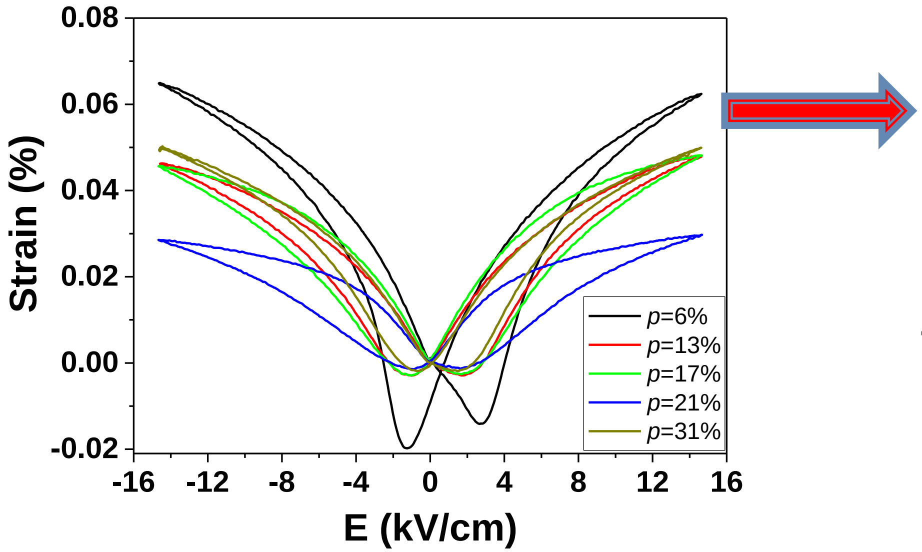
The piezoelectric energy harvesting figure of merit (FoM$_{ij}$) estimates the capability of BCTZ materials for mechanical energy harvesting applications $\Rightarrow$ **FOM$_{33}$ increases with increasing porosity until reaching the highest value of 18%.**

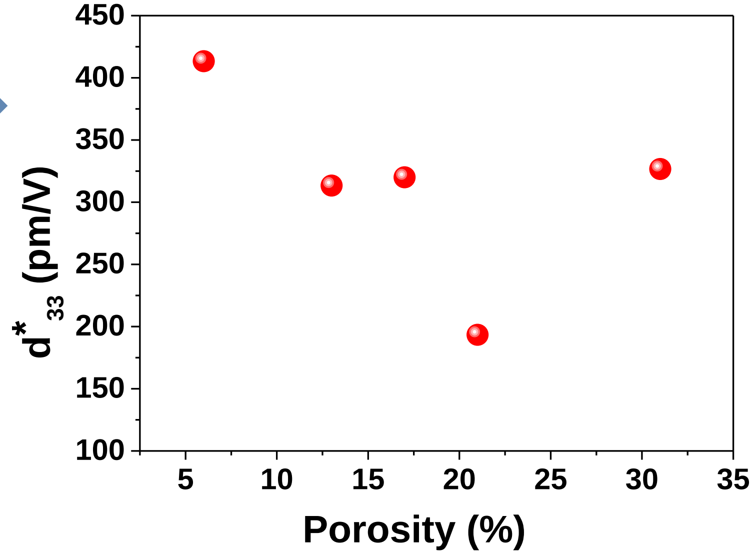
• Strain *vs.* Electric field (*E*) – inverse piezoelectric response

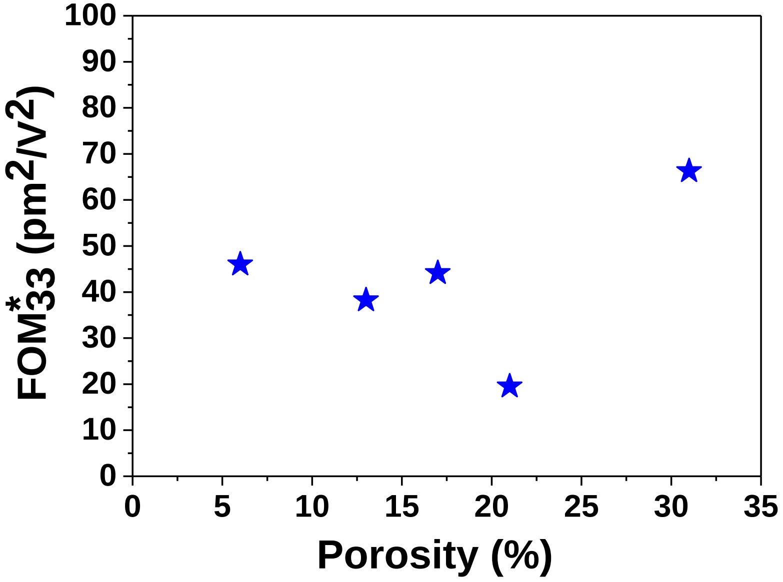
• Uniaxial pressed

(1-*x*)BCTZ+*x*PMMA









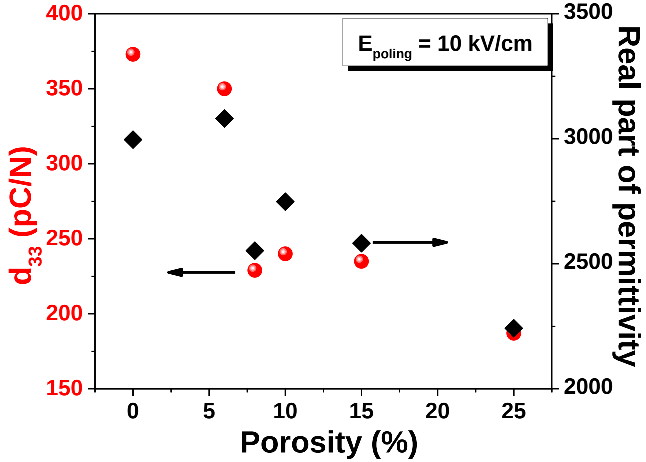
Piezoelectric harvesting *figure of merit*

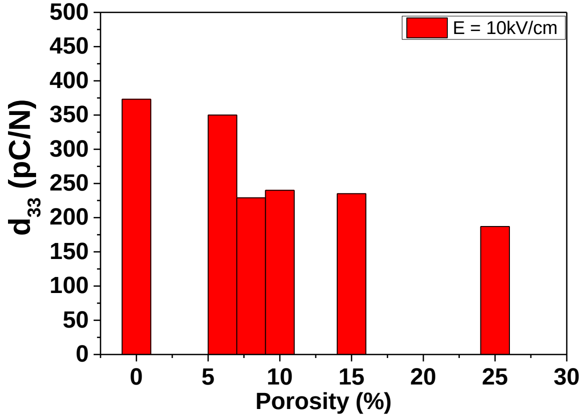
$$FOM_{ij} = d_{ij}^2/\varepsilon_{33}^T$$

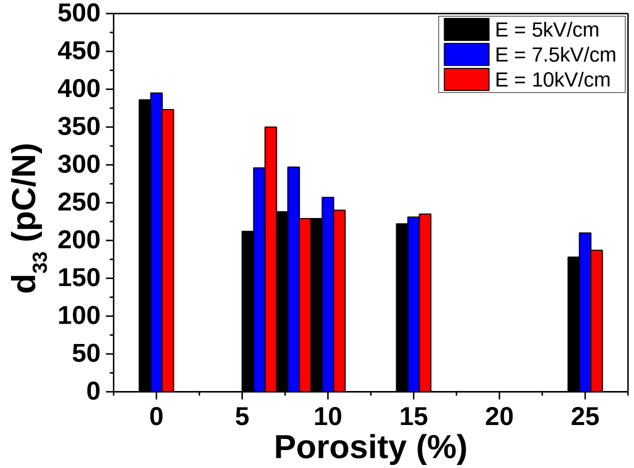
• Piezoelectric response and Figure of Merit (FOM)

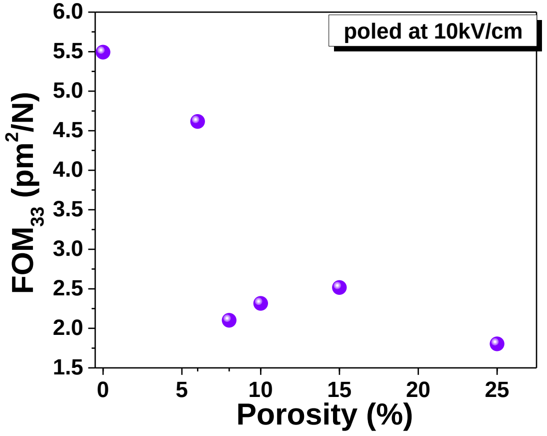
(1-x)BCTZ+xCNT

• Uniaxial pressed



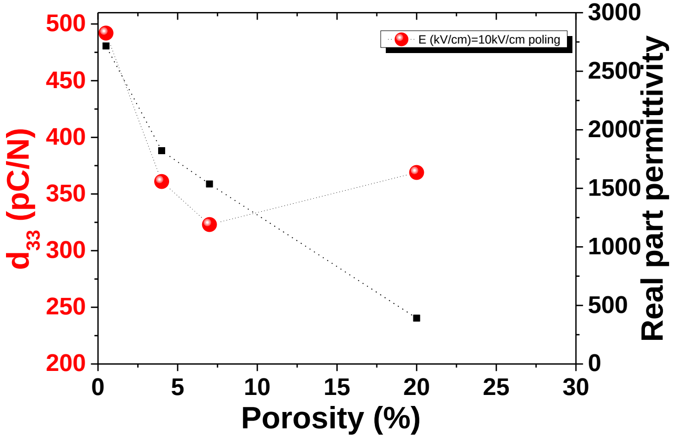


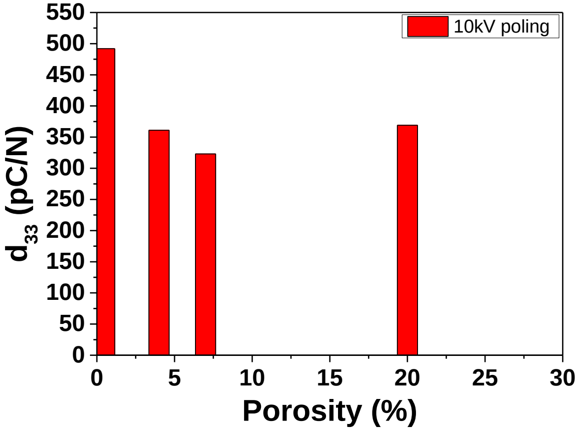


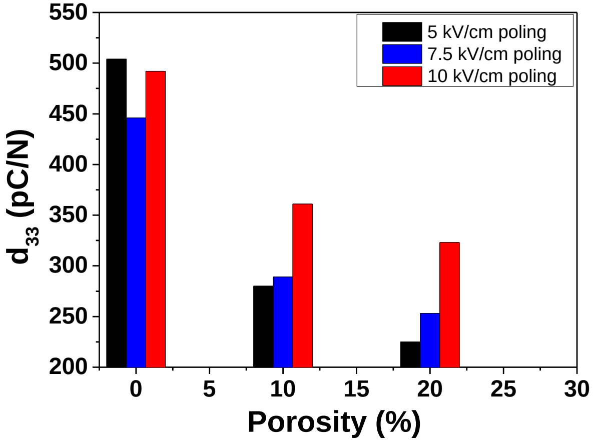


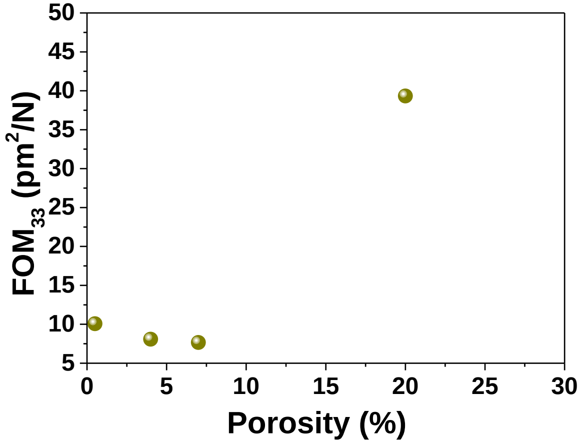
(1-x)BCTZ+xLF

• Uniaxial pressed









The deliverables realized within O2 during activities of the design, production and investigation of the effect of porosity on functional properties (dielectric, ferroelectric, nonlinear, piezoelectric and pyroelectric):

Demonstrating the benefits of introducing porosity in ferroelectric ceramics with the composition at MPB observed by:

(i) **the study of the effect of porosity on the dielectric properties at low electric fields; the investigation of the dielectric characteristics at different frequencies and temperatures showed that BCTZ ceramics produced with different degrees of porosity show a decrease in dielectric permittivity, a necessary condition for the selection of porous material for piezoelectric applications;**

(ii) **the study of the effect of porosity on the ferroelectric properties measured at high electric fields** ($E \cong$ 50kV/cm) showed that porous ceramics show a **decrease in remanent polarization due to the decrease in the volume of the ferroelectric matrix and the inhomogeneous distribution of the electric field in the sample**;

(iii) by polarizing the samples under an electric field of 10kV/cm, porous BCTZ ceramics showed **an increase in piezoelectric response, with high values of d_{33}=470pC/N for a porosity of 18%;**

(iv) **by controlling the composition and microstructure, BCTZ materials with variable porosity were produced, which showed a decrease in the dielectric constant, maintaining and even increasing the value of the piezoelectric coefficient d_{33}, which led to an improvement in the figure of merit of the piezoelectric response (FOM_{33}).**

✓ **Deliverables/results achieved in activ. A1.4, A1.5 - A2.4 - A3.4, Act 2.5, Act 2.6 – A3.5, A3.6, A3.7 are 5 sets of lead free ferroelectric ceramic ($BaTiO_3$ și BCTZ) with different porosity degrees, whose investigations, properties, interpretations, optimal results have been materialized in 4 ISI articles (published, accepted or under evaluation) and 1 patent application:**

1. ***Optimization of processing steps for superior functional properties of (Ba, Ca)(Zr, Ti)O3 ceramics***, C. E. Ciomaga, L. P. Curecheriu, V. A. Lukacs, N. Horchidan, F. Doroftei, R. Valois, M. Lheureux, M. H.e Chambrier and L. Mitoseriu, Materials 2022 15 (24), 8809 (ISI=3.4, Q2);
2. ***Porosity effects on the dielectric, ferroelectric and piezoelectric properties of (Ba, Ca)(Ti, Zr)O_3 ceramics***, N. Horchidan, L. P. Curecheriu, V.A. Lukacs, R. S. Stirbu, F. M. Tufescu, I. Dumitru, G. Stoian and C. E. Ciomaga, accepted Journal of the American Ceramic Society (2023) (ISI=3.9 Q1)
3. ***Influence of sintering temperature on electrical properties of SrTiO3-BaZrTiO3 ceramics for energy storage applications,*** I. Turcan, L.-P. Curecheriu, G. Stoian, C.-E.Ciomaga, and L. Mitoseriu, under review Ceramics International (2023) (ISI=5.2 Q1)
4. ***Preparation of porous BT-based ceramics by using MWCNT and exploring their functional properties***,F. Gheorghiu, N. Horchidan, V. Vasilache, I. Topala, F.-M. Tufescu, L. Mitoseriu, C.-E. Ciomaga, sent to Ceramics International (2023) (ISI=5.2 Q1)

Patent application:

1. ***Procedeu de obținere a ceramicilor poroase fără Pb cu performanțe piezoelectrice superioare pentru aplicații de recuperare de energie***, C.-E. Ciomaga, L.-P. Curecheriu, N. Horchidan, F. Gheorghiu, F.-M. Tufescu, OSIM CBI nr. A 00350/03.07.2023

O1. Material design using theoretical models

O2. Development of Pb-free porous ceramics with improved piezo-/pyroelectric FOMs

O3. Design of experimental devices for testing the produced and optimized porous ceramics (piezo- and pyroelectric sensors)

O3

O3. Design of experimental devices for testing the produced and optimized porous ceramics (piezo- and pyroelectric sensors)

Design and manufacture of experimental devices that will demonstrate:

(i) the detection and conversion of thermal and vibrational pulses and the collection capability of the proposed porous structures;

(ii) the benefits of introducing porosity into ferroelectric materials in terms of improving piezo/pyroelectric FOM.

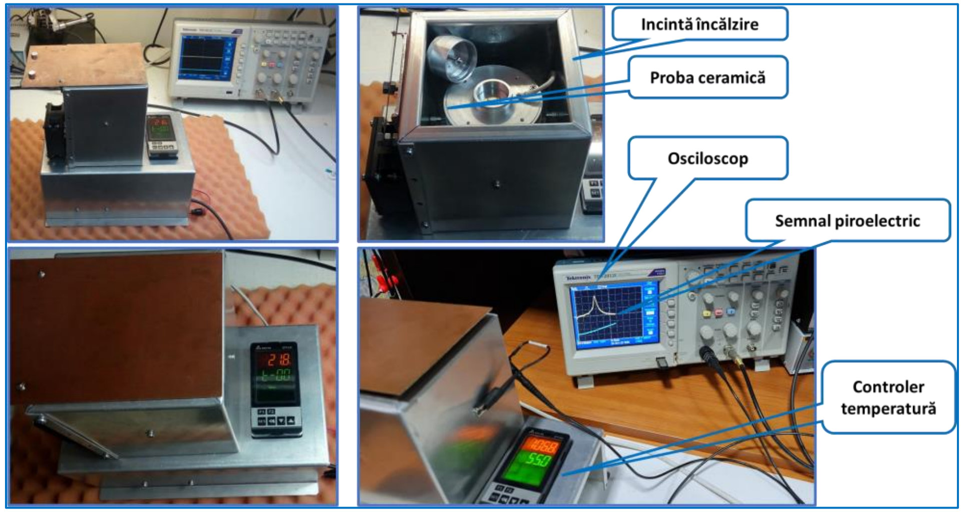
Novelty at national and international level

A1.6 Design and production of experimental devices for the detection, conversion, measurement of thermal and mechanical impulses for the collection of energy from different media.

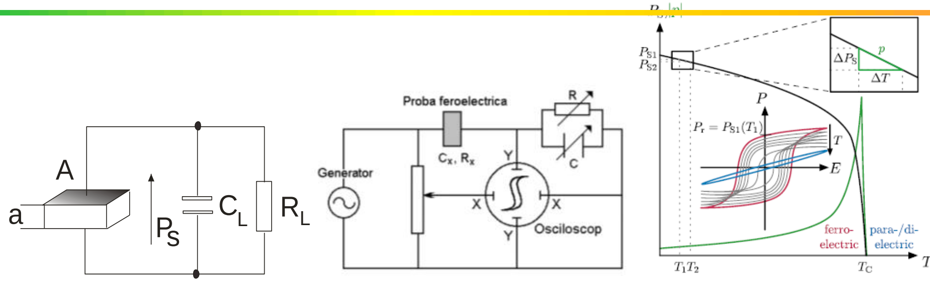
Act 2.7 Testing the experimental device with different types of input signal, using different piezoelectric porous ceramics for their integration as sensors in energy harvesting devices.

A3.8 Establishing protocols for piezoelectric and pyroelectric measurements in energy harvesting devices.

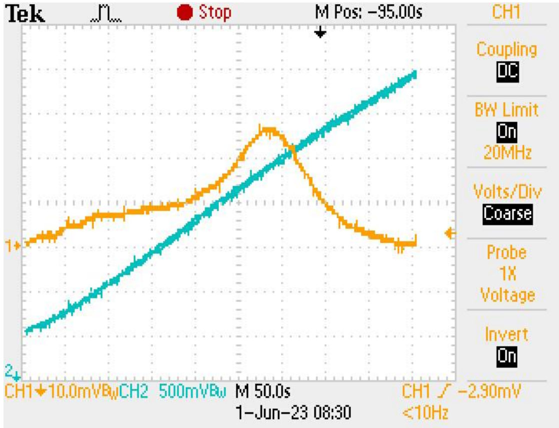
O3. Design of pyroelectric experimental devices for testing the produced and optimized porous ceramics



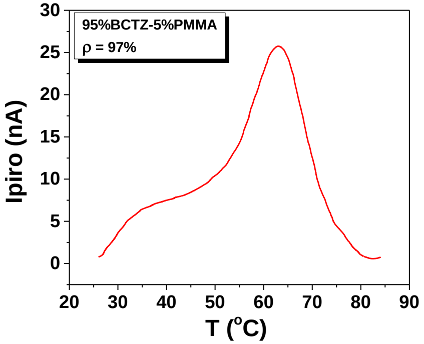
Experimental set-up for the determination of pyroelectric currents *and the calculation of the pyroelectric coefficient in dense ceramics with different degrees of porosity.*

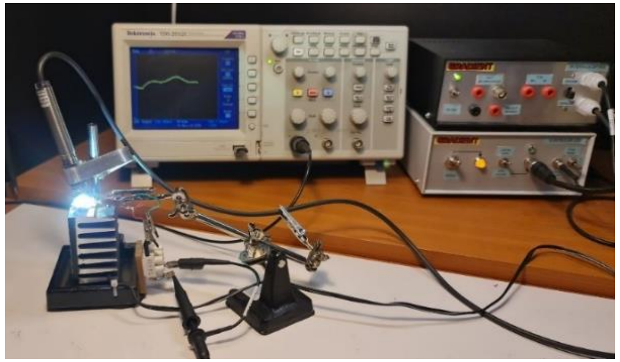


Schematic representation for pyroelectric coefficient measurements

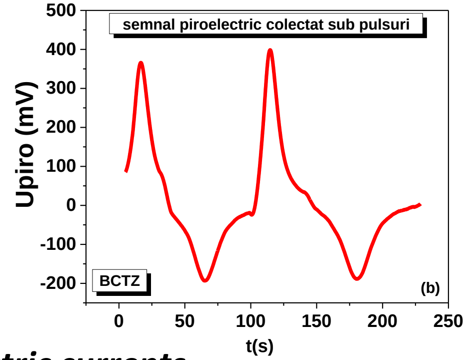


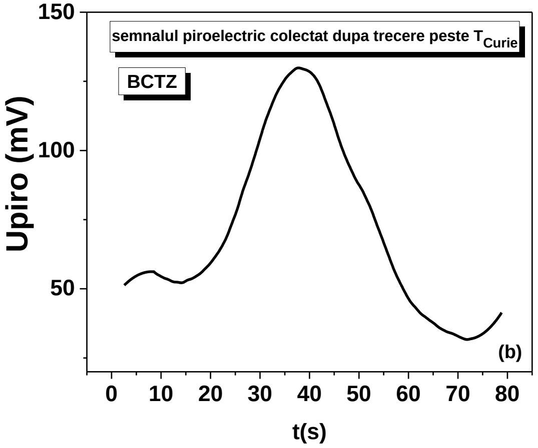
$$p = \frac{\partial P}{\partial T}$$ - **coeficientul piroelectric**

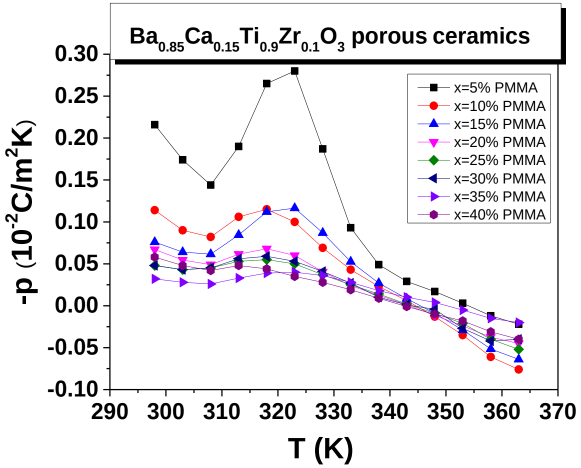




Experimental set-up for the measurement of pyroelectric currents dedicated to the collection of the electrical signal generated by BCTZ pyroelectric ceramics heated with power LEDs.

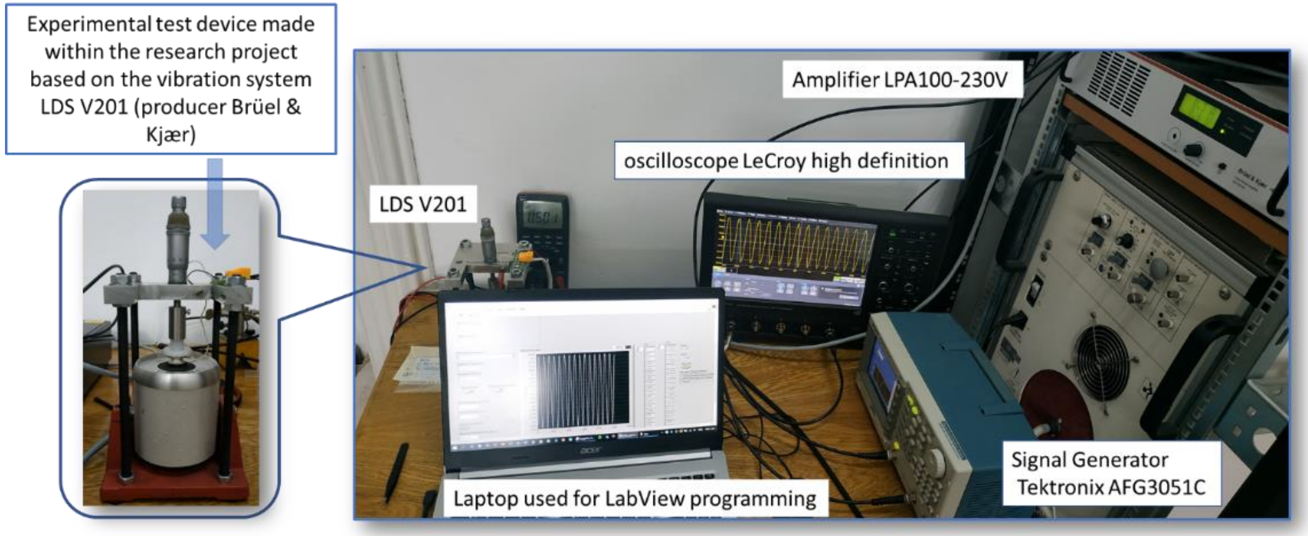




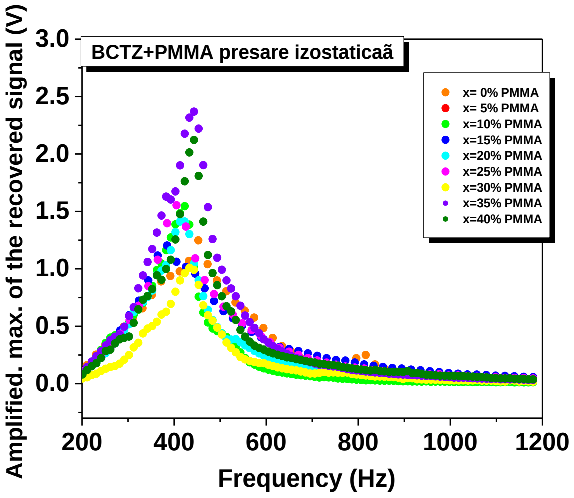


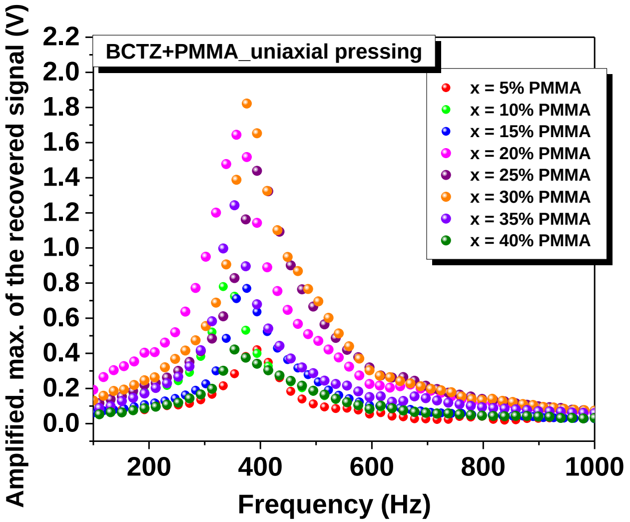
O3. 1. Experimental set-up for energy harvesting using mechanical vibration stimuli, for different frequencies

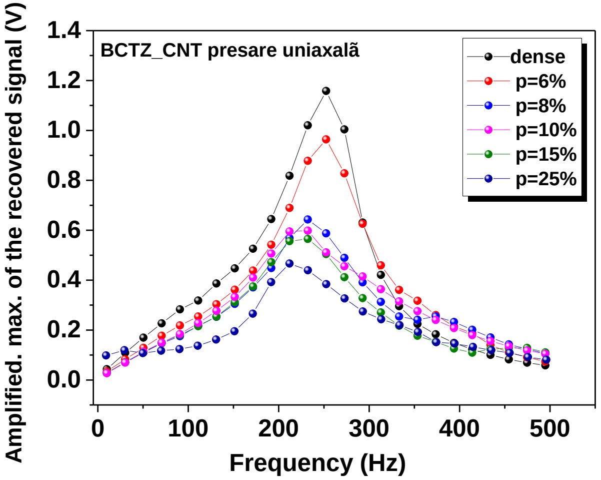
- ✓ **Experimental set-ups, techniques and measurement protocols have been designed and implemented** with the aim of detecting, converting and measuring thermal and mechanical impulses for porous ceramic materials, with a view to their use in devices for energy collection/recovery applications from different environments .



Set-up experimental

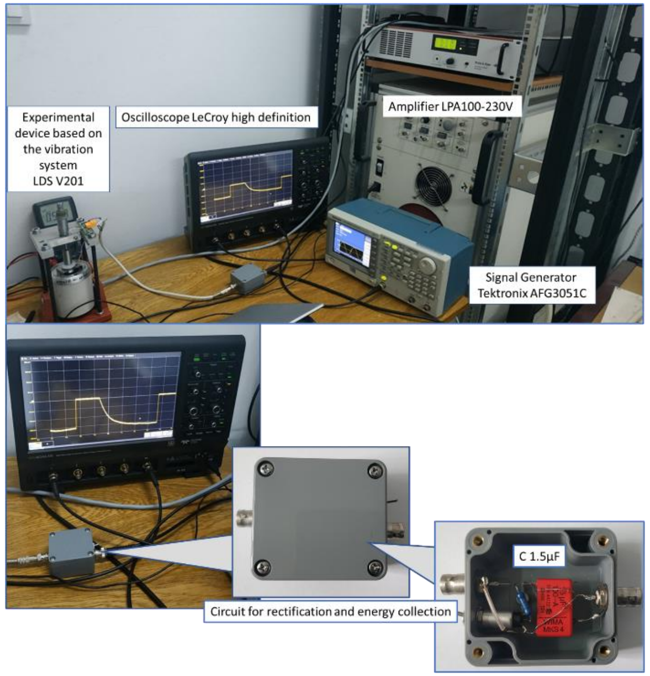




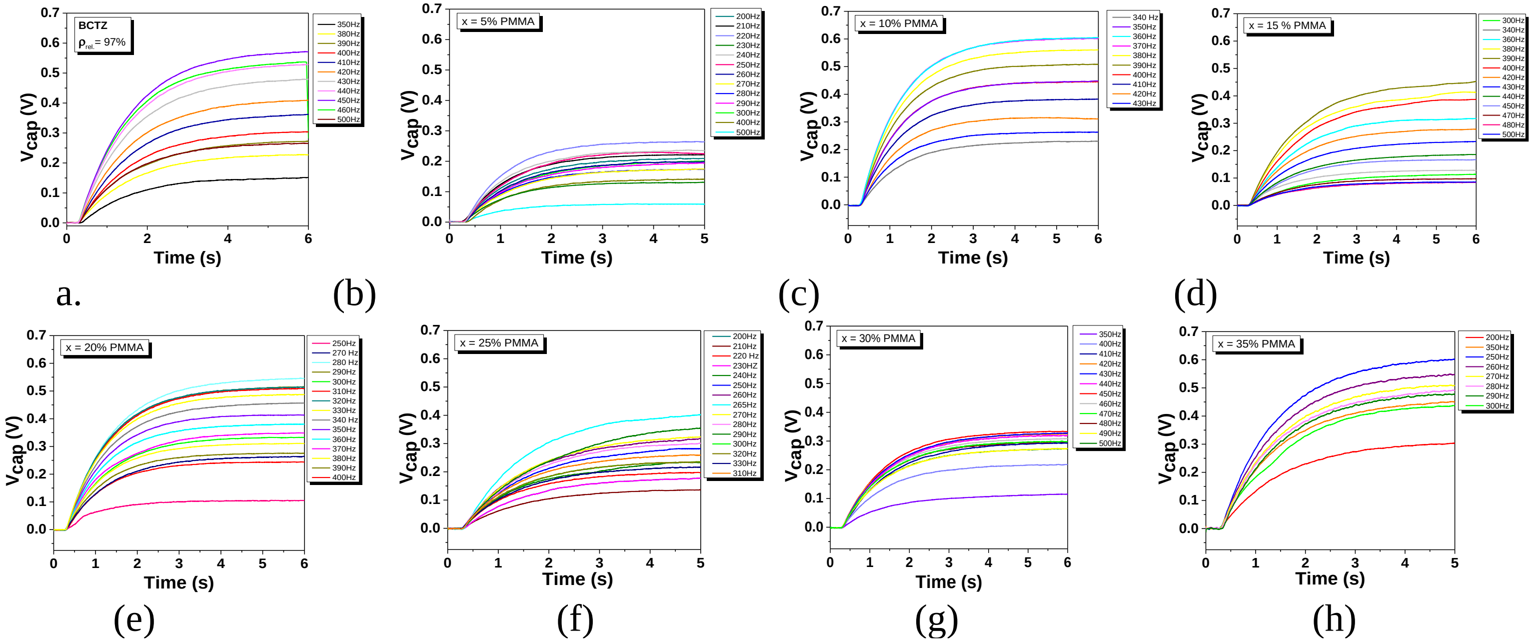


The values of the maximum amplitude of the signal recorded as a function of frequency for the porous BCTZ ceramics obtained by adding as a sacrificial material: PMMA - pressed isostatically; PMMA - uniaxially pressed and CNT- uniaxially pressed.

O3. 2. Experimental set-up for energy harvesting using mechanical vibration stimuli, for different frequencies

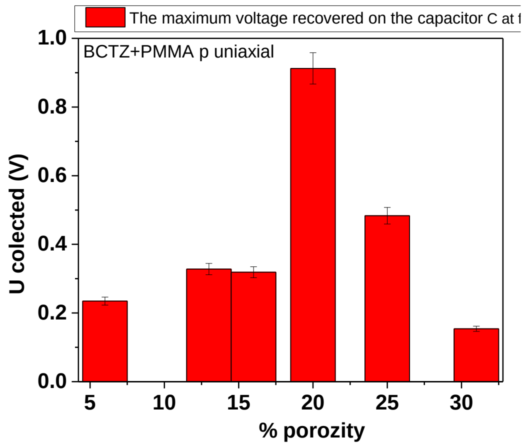


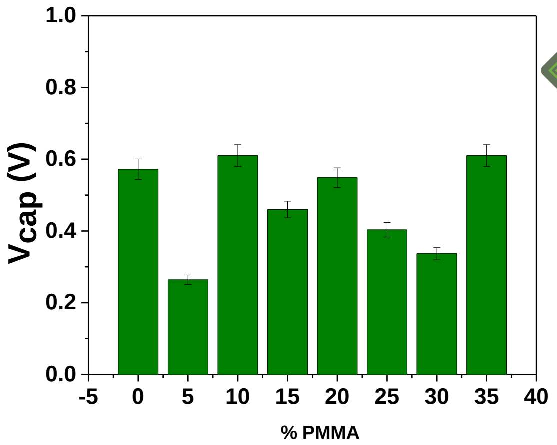
Experimental set-up made for harvesting resulting energy (capacitor charging) by applying mechanical vibration stimuli at fixed frequency on devices based on piezoelectric ceramic materials.



Value of charge voltage on capacitor C for BCTZ ceramics obtained by isostatic pressing with different additions of PMMA at different frequencies around the value for which maximum capacitor charge voltage was obtained (a-h) and maximum grouped values (i).

- ✓ **a fast charging (2s) of the capacitor which allows an increased efficiency of the system made for energy collection;**
- ✓ **maximum signal recovered: 0.6 V (isostatic)/0.9 V (uniaxial) for additions of 10% - 35% PMMA and frequencies range of (200-400)Hz.**





- **Deliverables/results achieved in activities A1.6, A2.7 și A3.8 are:**

(i) **Realization of experimental set-ups for testing ceramics with different degrees of porosity and collecting electrical energy converted from mechanical energy (mechanical vibration stimuli of a given frequency) as well as thermal energy (heating by thermal conduction and by power LED lighting);**

(ii) **selection of piezoelectric porous materials with real applicative possibilities for their integration as sensors in energy harvesting devices;**

(iii) **Protocols for measurements and collection of electrical energy converted from mechanical energy (stimuli of mechanical vibration of a given frequency) and thermal energy, respectively, using piezo/pyroelectric materials with different degrees of porosity, selected, for their potential to be integrate as sensors in energy harvesting devices.**

✓ **Deliverable/result achieved in activities A1.6, A2.7 și A3.8 was 1 patent application:**

Procedeu de obținere a ceramicilor poroase fără Pb cu performanțe piezoelectrice superioare pentru aplicații de recuperare de energie, C.-E. Ciomaga, L.-P. Curecheriu, N. Horchidan, F. Gheorghiu, F.-M. Tufescu, OSIM CBI nr. A 00350/03.07.2023.

Dissemination, management, coordination

✓ **8 ISI papers**

1. ***Modifications of structural, dielectric and ferroelectric properties induced by porosity in $BaTiO_3$ ceramics with phase coexistence***, L. Padurariu, L.-P. Curecheriu, C.-E. Ciomaga, M. Airimioaei, N. Horchidan, C. Cioclea, V.-A. Lukacs, R.-S. Stirbu, L. Mitoseriu, Journal of Alloys and Compounds 889, 161699 (2021) (ISI=5.316, Q1
2. ***Mesoscale Models for Describing the Formation of Anisotropic Porosity and Strain-Stress Distributions during the Pressing Step in Electroceramics***, R. S. Stirbu, L. Padurariu, F. F. Chamasemani, R. Brunner, and L. Mitoseriu, Materials 2022, 15, 6839 (ISI=3.4, Q2);
3. ***Optimization of processing steps for superior functional properties of (Ba, Ca)(Zr, Ti)O_3 ceramics***, C. E. Ciomaga, L. P. Curecheriu, V. A. Lukacs, N. Horchidan, F. Doroftei, R. Valois, M. Lheureux, M. H.e Chambrier and L. Mitoseriu, Materials 2022 15 (24), 8809 (ISI=3.4, Q2);
4. ***Analysis of local vs. macroscopic properties of porous $BaTiO_3$ ceramics based on 3D reconstructed ceramic microstructures***, L. Padurariu, F. F. Chamasemani, R. Brunner, L. P. Curecheriu, V. A. Lukacs, R. S. Stirbu, C. E. Ciomaga, L. Mitoseriu, Acta Materialia 255 (2023) 119084 (ISI=9,4 Q1)
5. ***Modeling of hysteretic response of porous piezo/ferroelectric ceramics***, R. S. Stirbu and L. Mitoseriu, Computational Materials Science (2023) (ISI=3.3 Q2)
6. ***Porosity effects on the dielectric, ferroelectric and piezoelectric properties of (Ba, Ca)(Ti, Zr)O_3 ceramics***, N. Horchidan, L. P. Curecheriu, V.A. Lukacs, R. S. Stirbu, F. M. Tufescu, I. Dumitru, G. Stoian and C. E. Ciomaga, accepted Journal of the American Ceramic Society (2023) (ISI=3.9 Q1)
7. ***Influence of sintering temperature on electrical properties of $SrTiO_3$-$BaZrTiO_3$ ceramics for energy storage applications,*** I. Turcan, L.-P. Curecheriu, G. Stoian, C.-E.Ciomaga, and L. Mitoseriu, under review Ceramics International (2023) (ISI=5.2 Q1)
8. ***Preparation of porous BT-based ceramics by using MWCNT and exploring their functional properties***, F. Gheorghiu, N. Horchidan, V. Vasilache, I. Topala, F.-M. Tufescu, L. Mitoseriu, C.-E. Ciomaga, sent to Ceramics International (2023) (ISI=5.2 Q1)

✓ **Patent application:**

1. ***Procedeu de obținere a ceramicilor poroase fără Pb cu performanțe piezoelectrice superioare pentru aplicații de recuperare de energie***, C.-E. Ciomaga, L.-P. Curecheriu, N. Horchidan, F. Gheorghiu, F.-M. Tufescu, OSIM CBI nr. A 00350/03.07.2023

Dissemination, management, coordination

- ✓ **pagina web a proiectului: https://www.uaic.ro/enginpor/**

- ✓ **Participation in 11 international conferences and 6 national conferences/workshops with 29 presentations of which 2 as invited, 19 oral and 8 poster**

- ✓ **on-line workshop Romania-Polonia: *Efectul porozității asupra răspunsului piezoelectric în ceramicile BCTZ***

Equipment purchases :

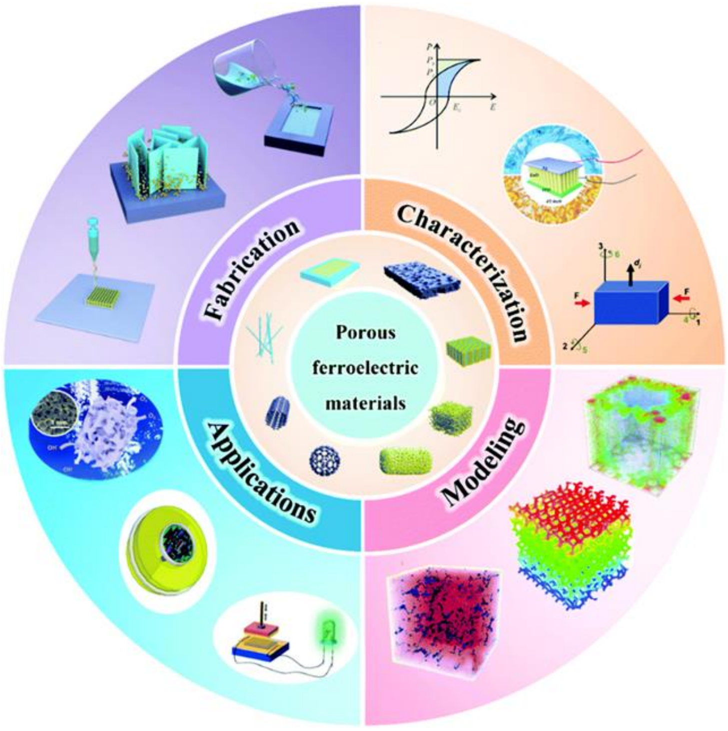
- *Lyophilizer – system for extracting water from powders;*
- *Powder sieving machine;*
- *Vibration system – in a wide range of frequencies,*
- *Ultrasonic bath – for cleaning ceramic samples;*
- *Tubular furnace - used in thermal treatments for obtaining ceramics as well as for surface treatment of ceramics whose surfaces are to be investigated with microscopy techniques;*
- *Manual press – for pressing powders;*
- *Chemical reagents;*
- *High performance computers.*

All activities provided for in the implementation plan of the PN-III-P4-ID-PCE-2020-1988 project were successfully achieved.

Conclusions

Porous Pb-free ceramics with different pore geometries have been produced, exhibiting improved piezoelectric coefficient and Figure of Merit FOM_{33}

- ✓ **The design and fabrication of Pb-free porous ferroelectric materials have demonstrated that a certain level of porosity can be beneficial to the piezoelectric response.**
- ✓ **Porous ceramics can be used as sensors in devices for electrical energy harvesting applications.**



- M. Yan, et al., Energy Environ. Sci., (2021) 14, 6158