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

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Year II (2022) - Summary

In this 2nd stage, the activities from the project implementation plan which have been accomplished are: >A2.1-3 Study of the impact of electric field distribution on the dielectric, piezo/pyroelectric response, P(E) and tunability for different pore shapes (activ. will continue in 2022).

>A2.2 Design of piezo/pyroelectric ceramic microstructures, using theoretical models, with improved FOM (activ. will continue in 2022).

>A2.3 Theoretical validation of functional properties (dielectric, ferroelectric properties and piezo/pyroelectric properties) for realistic microstructures (activ. will continue in 2023).

>A2.4 Production of Pb-free porous ceramics (with different types of pore connectivity) (activ. will continue in 2022).

>A2.5 Microstructural characterization of Pb-free porous ceramics; selection of structures with superior piezopyroelectric response to improve FOM.

A2.6 Study of the effect of porosity on dielectric properties in low and high electric fields (activ. will continue in 2023).
A2.7 Testing of the experimental set-up with different types of input signal, using different porous piezoelectric ceramics for their integration as sensors in energy collection devices.

>A2.8 Coordination, management and dissemination of the results obtained.

Scientific and technical description of the activities and results

Year II - 2022

Design, preparation, optimization, microstructural and functional characterization of Pb-free porous piezoelectric microstructures with improved FOM. Testing of prepared porous ceramics in the design experimental set-ups.

- A2.1-3 Study of the impact of electric field distribution on the dielectric, piezo/pyroelectric response, P(E) and tunability for different pore shapes (activ. will continue in 2022). Design of piezo/pyroelectric ceramic microstructures, using theoretical models, with improved FOM (activ. will continue in 2022). Theoretical validation of functional properties (dielectric, ferroelectric properties and piezo/pyroelectric properties) for realistic microstructures (activ. will continue in 2022).
- By using analytical and numerical models it was demonstrated the influence of the pore shapes, obtained using different pressing steps, on mechanical, piezelectric properties.
 - > Formation of Anisotropic Porosity and Strain-Stress Distributions during the Pressing Step in Electroceramics





Position of the presented inclusions relative to a cylinder axis OZ

Illustration of the main stresses in a cylindrical body (**a**); radial and tangential stresses on an insulated volume element (**b**); calculation of the external radius (**c**); illustration of the mechanical equilibrium conditions (**d**).

 Theoretical calculation and simulations results – for a simulated microstructures with spherical inclusions for creation of pores into a ceramic matrix,

pressing.

(d)

-25 0 25 50 75 100 Angle (°)

(d)

100 -75 -50



Systems with 10, 50, 500 and 950 circular inclusions (**a**) and the corresponding simulated microstructures after the deformation by <u>isostatic pressing</u> (**b**).



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 <u>uniaxial pressing</u>: (**a**) before pressing, (**b**) after pressing and deformation; (**c**) uniaxially entirely deformed structure; (**d**) angular distribution of inclusions derived for uniaxial



Comparative plot of aspect ratio distributions of the soft phase for isostatic and uniaxial pressing

The main results of this study were published in 1 ISI paper, Materials 2022, 15, 6839 Q1 (ISI=3,748); • Theoretical simulations - porosity effect on piezoelectric response in porous ferroelectric materials with different shape of pores:



Porous systems with different shape of pores - The field direction is applied along the vertical axis Oz, and the strain is measured along the same axis, to evaluate the piezoelectric response (d_{33}) .



Piezoelectric strain as a function of porosity for a variable no. of inclusions: (a, b) spherical, (c) elongated ellipsoids



a clear tendency to obtain a local maximum of the piezoelectric strain, and of d₃₃ respectively, for ~10% porosity, followed by a decrease with increasing porosity.

• Design of piezoelectric ceramic microstructures - Study of the impact of electric field distribution on the dielectric response for porous microstructures using theoretical Finite Element Model (FEM)



The dielectric properties derived by using FEM were discussed in comparison with experimental data of $BaTiO_3$ porous microstructure.

(a) Local potential on the bulk ceramic of BT81 (subsystem S1), as determined by FEM analysis for three different boundary conditions (electric field applied along the Ox, Oy and Oz directions, respectively, in parallel plate capacitor geometry) and (b) the corresponding local field distributions.

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.



Computed permittivity vs. porosity of the eight sub-systems corresponding to the BT89, BT81 and BT74 porous ceramics as derived from FEM analysis. The electric field was applied along the Ox, Oy, Oz axes.

Deliverables/results achieved by A2.1-3 activities are:

- (i) it was demonstrated by analytical and numerical calculation that both by 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 of ~10% 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 electric field distributions and dielectric response for different porous microstructures were performed, and these were validated by comparing them with experimental results obtained on porous BaTiO₃ ceramics.

Indicators of results of the A2.1-3 activities are:

2 ISI papers:

- 1) R.S. Stirbu, L. Padurariu, F.F. Chamasemani, R. Brunner, L. Mitoseriu, Mesoscale models for describing the formation of anisotropic porosity and strain-stress distributions during the pressing step in electroceramics, Materials 15, 6839 (2022) (in collaboration with the PN-III-P1-1.1 project -TE-2019-1929) Q1 (ISI=3.748);
- 2) L. Padurariu, F.F. Chamasemani, R. Brunner, L. Curecheriu, V.A. Lukacs, R.S. Stirbu, C.E. Ciomaga, L. Mitoseriu, Analysis of local vs. macroscopic properties of porous BaTiO3 ceramics based on 3D reconstructed ceramic microstructures, under review in Acta Materialia (2022), Q1 (ISI=9,202).

Dissemination of these results was made in the frame of 1 international conference.

> A2.4 Production of Pb-free porous ceramics (with different types of pore connectivity) (activ. will continue in 2022).

At this stage, it was prepared the 3 sets of Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O₃ ferroelectric ceramics with different degrees of porosity created by the BURN-OUT sintering technique.

Manufacturing of ceramics with different degrees of porosity using different techniques, synthesis, and sintering steps was realized by using different sacrificial materials:

(i) spherical particles of polymethyl methacrylate (PMMA), pressed isostatically and uniaxially;

(ii) (ii) carbon nanotubes (MWCNTs)



Porosity vs. addition of different sacrificial templates used to create ceramics with different degrees of porosities Deliverables/results achieved by A2.4 activity are:

• at least 3 sets of BCTZ type ceramic samples with different degrees of porosity were prepared (at least 8 samples/set each) from which they were selected and investigated in the project activities.

Dissemination of the A2.4 activity was achieved by presenting the results in **3 national and 5 international conferences/workshops.**

A2.5 Microstructural characterization of Pb-free porous ceramics; selection of structures with superior piezo/pyroelectric response to improve FOM.

The microstructure analysis of the ceramics produced within the project was carried out as part of this activity, using the Scanning Electron Microscopy (SEM) technique.



SEM microstructures of porous BCTZ ceramics obtained by the addition of PMMA microspheres and isostatic pressing.



SEM microstructures of BCTZ porous ceramics obtained by the addition of CNTs



SEM microstructures of porous BCTZ ceramics obtained by the addition of PMMA microspheres and uniaxial pressing.

Deliverables/results achieved by A2.5 activity are:

microstructures with different degrees of porosity, with different pore geometries, from spherical to elongated, elliptical shapes, and microstructural connectivity of the active ferroelectric phase of type (0-3), (1-3) and even (2-2).

Dissemination of the A2.5 activity in the frame of **4 national** workshops/conferences and 5 international conferences.

> A2.6 Study of the effect of porosity on dielectric properties in low and high electric fields (activ. will continue in 2023)

For the electrical measurements, Ag electrodes were deposited on the plane-parallel surface of the BCTZ ceramic samples, followed by annealing at 200 °C for 2 hours. Dielectric measurements at low fields (1V) were performed at room temperature using a Solartron 1260 (Solartron Analytical, Hampshire, UK) for frequencies between 1 Hz and 1 MHz and at temperatures between 20÷150°C using an LCR bridge Hameg HM8118.

• Dielectric properties at low fields



> Permittivity decreases with increasing porosity, at T_{room}, for all porous BCTZ ceramics

> All the samples show good dielectric properties with small losses (< 0.025 for kHz frequency range) and high dielectric constant (> 2500) even for a 31% porosity level;



Ferroelectric properties at high electric fields



Hysteresis loops, P(E), of BCTZ porous ceramics obtained by adding particles of (a) PMMA, isostatically pressed, (b) PMMA, uniaxially pressed, and (c) CNTs, uniaxially pressed

The remnant polarization decreased with an increase in porosity due to the reduced amount of ferroelectric ceramic and the additional depolarization factor determined by the shape of the pore and the associated electric field distribution around the pore.

Piezoelectric properties

The samples were poled at T_{room} at E=10kV/cm for 10min

100

0

10 20 30



Piezoel. Coefficient d_{33} increase, while the permittivity decrease with the increase of porosity requirements for materials with enhanced FOM

40 50 60 70 80 90 100

Porosity (%)

Piezoelectric energy harvesting • Figure of Merit (FOM)



 $FOM_{ij} = d_{ij}^2 / \varepsilon_{22}^T$

 d_{ii} -piezoelectric strain coefficient (the subscripts denote the direction of applied stress (*j*) with respect to the poling direction (i)) ε_{ii}^{T} - the relative permittivity.

Porous BCTZ ceramics present an increase of piezoelectric FOM, with \succ decreasing permittivity and a high value of FOM for 18% porosity.

Deliverables/results achieved by A2.6 activity are:

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

- studying the effect of porosity on the dielectric properties at weak electric fields; the investigation of the dielectric characteristics at different frequencies and temperatures showed that BCTZ samples 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 porosity effect on the ferroelectric properties measured at intense electric fields (E>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 poling 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, the maintenance and even increasing of d_{33} , which led to an improvement of the figure of merit of the piezoelectric response (FOM₃₃).

Dissemination and indicator of results for A2.6 activity:

2 ISI papers:

- Cristina E. Ciomaga, Lavinia P. Curecheriu, Vlad A. Lukacs, Nadejda Horchidan, Florica Doroftei, Renaud Valois, Mégane Lheureux, Marie Hélène Chambrier and Liliana Mitoseriu, *Optimization of processing steps for superior functional properties of (Ba, Ca)(Zr, Ti)O₃ ceramics*, accepted Materials 2022, Q1 (ISI=3,784) (collaboration with PNIII-P3-3.1-PM-RO-FR-2019-0069 și PN-III-P1-1.1-TE-2019-1689);
- 2) C. E. Ciomaga, L. P. Curecheriu, N.Horchidan, V. A. Lukacs, G. Stoian, and L. Mitoseriu, *Porosity effects on the dielectric, ferroelectric and piezoelectric properties of (Ba, Ca)(Ti, Zr)O3 ceramics*, sent to Journal Alloys and Compound (2022), Q1 (ISI=6,371).

- The results were presented at 4 national and 5 international conferences/workshops.

> A2.7 Testing of the experimental set-up with different types of input signal, using different porous piezoelectric ceramics for their integration as sensors in energy collection devices.

• Functionalization of experimental set-up for energy harvesting using mechanical vibration stimuli, for different frequencies, with the aim of testing dense and porous piezoceramic materials.



Maximum signal amplitude values recorded as a function of frequency for porous BCTZ ceramics obtained by adding as sacrificial material: (a) CNT- uniaxially pressed, (b) PMMA - isostatically pressed, and (c) PMMA - uniaxially pressed.

BCTZ porous piezoelectric ceramics were tested with different types of signal (variable frequency or amplitude), and the measurements were programmed using the LabView program (variation of frequency, signal amplitude, number of recorded points, etc.)

- all porous BCTZ ceramics generated signal and the maxima are around the frequency of 450Hz, the characteristic frequency of the resonator assembly built on the basis of the LDS V201 vibration system.
- with increasing porosity, a broadening of the frequency dependence of the signal is obtained, which provides increased possibilities for energy harvesting from mechanical vibration stimuli

 Experimental set-up for energy recovery resulting from the application of fixed-frequency mechanical vibration stimuli on devices with piezoelectric ceramic materials



Circuit for rectification and energy collection

C = 1.5µF

- calibration of the system and performance testing of the set-up by using a BCTZ ceramic sample with high



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





- a maximum recovery of around 0.6 V was observed for the additions of 10% PMMA (12% porosity) and 35% PMMA (18% porosity) and (200-400)Hz frequency range.
- it is noted the very fast charging (2s) of the capacitor, which allows increased efficiency of the system created for energy collection.

• Deliverables results of A2.7 activity are:

- (i) making set-ups for testing and collecting electrical energy converted from mechanical energy (mechanical vibration stimuli of a given frequency)
- (ii) selecting piezoelectric porous materials with real application possibilities for their integration as sensors in energy harvesting devices. The obtained values are at the level of those reported in the literature.

Dissemination of these results will be the subject of a **patent proposal**.

> A2.8 Coordination, management and dissemination of the obtained results

• The project web page has been updated: <u>https://www.uaic.ro/enginpor/</u>

• Dissemination activities were carried out through the publication of **4 ISI articles** and participation in **5 international conferences and 4 national conferences/workshops with 9 oral presentations and 4 posters**.

• Equipment purchases were made:

Ultrasonic bath – for cleaning ceramic samples;

Tubular furnace - used in thermal treatments to obtain ceramics as well as for surface treatment of ceramics whose surfaces are to be investigated with microscopy techniques;

Manual press – for pressing powders, necessary for carrying out the research and dissemination activities within the project.

> A2.8 Coordination, management, dissemination.

- 4 ISI papers:
- <u>R. S. Stirbu</u>, <u>L. Padurariu</u>, F. F. Chamasemani, R. Brunner, and <u>L. Mitoseriu</u>, *Mesoscale Models for Describing the Formation of Anisotropic Porosity and Strain-Stress Distributions during the Pressing Step in Electroceramics*, Materials 2022, 15, 6839, Q1 (ISI=3,748) (collaboration with PN-III-P1-1.1-TE-2019-1929).
- <u>C. E. Ciomaga, L. P. Curecheriu</u>, <u>V. A. Lukacs</u>, <u>N. Horchidan</u>, F. Doroftei, R. Valois, M. Lheureux, M. H. Chambrier and <u>L. Mitoseriu</u>, *Optimization of processing steps for superior functional properties of (Ba, Ca)(Zr, Ti)O₃ ceramics*, accepted Materials 2022 Q1 (ISI=3,748) (collaboration with PNIII-P3-3.1-PM-RO-FR-2019-0069 și PN-III-P1-1.1-TE-2019-1689);
- L. Padurariu, F.F. Chamasemani, R. Brunner, L. Curecheriu, V.A. Lukacs, R.S. Stirbu, C.E. Ciomaga, L. Mitoseriu, Analysis of local vs. macroscopic properties of porous BaTiO₃ ceramics based on 3D reconstructed ceramic microstructures, sent to Acta Materialia (2022), Q1 (ISI=9,202).
- 4. <u>C. E. Ciomaga</u>, L. P. Curecheriu, N.Horchidan, V. A. Lukacs, G. Stoian, and L. Mitoseriu, *Porosity effects on the dielectric, ferroelectric and piezoelectric properties of (Ba, Ca)(Ti, Zr)O₃ ceramics*, sent to Journal Alloys and Compound (2022), Q1 (ISI=6,371).
- The scientific results were presented at 5 international conferences and 3 national conferences/workshops (9 oral and 4 poster presentations):
- C. E. Ciomaga, L. Padurariu, L. P. Curecheriu, Nadejda Horchidan, Florin M. Tufescu and Liliana Mitoseriu, *Design and functional properties of porous BaTiO₃based materials with enhanced piezoelectric Figure of Merit: experiment and modeling*, European Advanced Materials Congress, IAAM Onsite-online, 25June-02July, Genoa, Italy (oral presentation and Session chair of Composite&Ceramic Materials) (<u>https://www.iaamonline.org/advanced-materials-congress</u>)
- C. E. Ciomaga, L. P. Curecheriu, V.A. Lukacs, N. Horchidan, M. Lheureux, M. H. Chambrier and L. Mitoseriu, *Comparative study of phase composition and properties of Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O₃ ceramics prepared by different synthesis methods, IEEE ISAF-PFM-ECAPD 2022 Conference, 27June-01July, Tours, France (poster presentation) (<u>https://2022.ieee-isaf.org/</u>)*
- C. E. Ciomaga, L. P. Curecheriu, L. Padurariu, A. V. Lukacs, N. Horchidan, George Stoian and L. Mitoseriu, *Influence of porosity on dielectric, ferroelectric and pyro-, piezoelectric properties for Ba_{0.85}Ca_{0.15}Ti_{0.90}Zr_{0.10}O₃ porous ceramics, "Ceramics in Europe" Conference2022, ICC9, XVIIECerS, XVIII ElectroCeramics, 10-14 July 2022, Krakow, Poland (oral presentation and Session chair) (<u>https://2022.ieee-isaf.org/</u>)*

All the activities of this II stage (2022) have been successfully completed.

4. C.E. Ciomaga, N. Horchidan, F. M. Tufescu, L. P. Curecheriu, and Liliana Mitoseriu, *Investigation of energy harvesting properties in porous* Ba_{0.85}Ca_{0.15}Ti_{0.90}Zr_{0.10}O₃ ceramics with enhanced piezoelectric figure of merits, "Ceramics in Europe" Conference2022, ICC9, XVIIECerS, XVIII ElectroCeramics, 10-14 July 2022, Krakow, Poland (poster presentation) (<u>https://www.ceramicsineurope2022.org/</u>)

5. C. E. Ciomaga, L. P. Curecheriu, N. Horchidan, F. M. Tufescu, L.Padurariu, and L. Mitoseriu, *Manufacture and functional characterization of porous Ba*_{0.85}*Ca*_{0.15}*Ti*_{0.90}*Zr*_{0.10}*O*₃ *ceramics for piezoelectric energy harvesting applications*, Seventh International Conference on Multifunctional, Hybrid and Nanomaterials, 19-22 October 2022, Genoa, Italy (oral presentation) (<u>https://www.elsevier.com/events/conferences/international-conference-on-multifunctional-hybrid-and-nanomaterials/programme</u>)

6. R. S. Stirbu, L. Padurariu, V. A. Lukacs, L. Mitoseriu, *Mesoscale models for strain-stress distributions in anisotropic porous BaTiO3 ceramics*, Seventh International 2022. Conference Multifunctional, Hybrid and Nanomaterials, 19 -22 October Genoa, Italy (poster presentation) on (https://www.elsevier.com/events/conferences/international-conference-on-multifunctional-hybrid-and-nanomaterials/programme)

7. C. E. Ciomaga, *Ingineria materialelor ceramice poroase fără plumb pentru obținerea de senzori piezo-, piroelectrici cu aplicații de colectare de energie,* Sesiune de comunicari in cadrul proiectului PDI-PFE *Susținerea competitivității în cercetare-dezvoltare și inovare prin dezvoltarea capacității instituționale a Universității "Alexandru Ioan Cuza" din Iași,* 25 March 2022, Iasi, Romania (oral presentation) (<u>https://www.uaic.ro/uaic-inov-imp2-os5-a2/</u>)

8. M. Osman, C. E. Ciomaga, L. Mitoseriu, *Preparation and electrical properties of BaTiO₃ - based porous ceramics*, Pentagonul Facultatilor de Fizica, 24-26July, Magurele, Romania (oral presentation) (<u>http://fizicieni.ro/pentagon.php</u>)

9. F. Gheorghiu, N. Horchidan, V. Vasilache, and C. E. Ciomaga, *Preparation and electrical properties of porous (Ba,Ca)(Ti,Zr)O₃ ceramics using MWCNT templates,* "Researcher day at UAIC", 27th October 2022, Al. I. Cuza University of Iasi, Romania (poster presentation)(<u>https://www.uaic.ro/uaic-inov-imp2-os6-a1-1/</u>)

10. C. E. Ciomaga, L. P. Curecheriu, L. Padurariu, N. Horchidan, A. V. Lukacs and L. Mitoseriu, *The influence of porosity on the structural and electrical properties of ferroelectric ceramics*, International Workshop on Advanced Materials and Applications, 28 October 2022, Faculty of Physics, Al. I. Cuza University of Iasi, Romania (oral presentation) (<u>https://www.phys.uaic.ro/wp-content/uploads/2022/10/Dies-Academici-Festivi-Universitatis-Iassiensis-2022.pdf</u>)

11. F. Gheorghiu, N. Horchidan, C. E. Ciomaga, *Porous (Ba, Ca)(Ti, Zr)O₃ ceramics using MWCNT templates for piezoelectric,* International Workshop on Advanced Materials and Applications, 28 October 2022, Faculty of Physics, Al. I. Cuza University of Iasi, Romania (oral presentation) (<u>https://www.phys.uaic.ro/wp-content/uploads/2022/10/Dies-Academici-Festivi-Universitatis-Iassiensis-2022.pdf</u>)

12. M. Osman, C. E. Ciomaga, L. Mitoseriu, *Preparation and electrical properties of BaTiO₃ - based porous ceramics,* International Workshop on Advanced Materials and Applications, 28 October 2022, Faculty of Physics, Al. I. Cuza University of Iasi, Romania (oral presentation) (<u>https://www.phys.uaic.ro/wp-content/uploads/2022/10/Dies-Academici-Festivi-Universitatis-Iassiensis-2022.pdf</u>)

13. M. Osman , C. E. Ciomaga , L. P. Curecheriu , N. Horchidan, L. Mitoseriu, *Beneficiile introducerii porozitătii în ceramici feroelectrice pe bază de BaTiO₃ pentru aplicatii piezoelectrice, FARPHYS 2022*, 4 November 2022, Faculty of Physics, Al. I. Cuza University of Iasi, Romania (oral presentation) (<u>https://www.phys.uaic.ro/index.php/cercetare-conferinte-cercetare-conferinte-cercetare-2022/</u>)

All the activities of this II stage (2022) have been successfully completed.