New Materials, Compounds and Applications
Vol.9, No.2, 2025, pp.271-281
https://doi.org/10.62476/nmca.92271

LEAD-FREE PIEZOELECTRIC DEVICE WAS DEVELOPED USING NANOPARTICLES MATERIALS AND GREEN CHEMISTRY

Pedro Vera-Serna[1*], José Agustín Palmas-León[1], Francisco Raúl Barrientos-Hernández[2], Felipe Nerhi Tenorio-Gonzalez[1], Iván Ricardo Barajas-Rosales[3], Graciela Margarita Cetina-Quijano[1]

[1]Universidad Politécnica de Tecámac, Tecámac, Mexico
[2]Universidad Autónoma del Estado de Hidalgo, Mineral de la Reforma, Mexico
[3]Instituto Tecnológico de Pachuca, Pachuca de Soto, Mexico

Abstract. Piezoelectric lead-free pill was developed with ceramics powders synthesized with green chemistry (high energy milling route) using Bi_2O_3, Na_2CO_3 and TiO. The structural characterization of material was with X-Ray Diffraction technique and it was possible to identify the synthesis of NBT structure. The evaluations were using values of X=0.01 to X=0.1 in $(Bi_{0.5-x}Na_{0.5+x})\ TiO_3$. The Rietveld method lets determine lattice parameters and crystal size. The morphology was observed with Scan Electron Microscope showing irregular shapes. In the study it was necessary to compare the sizes particles distribution to determine the possible justification on properties with the nanoparticles detected on diverse samples. The response in voltage was evaluated with pill, Arduino system, software and computer getting show a piezoelectric material.

Keywords: *Piezoelectric material, high energy milling, nanoparticles, lead-free advanced ceramic, NBT ceramic.*

Corresponding Author: *Pedro Vera-Serna, Universidad Politécnica de Tecámac, Tecámac, Mexico, Tel.: +5215559388670, e-mail: pedrovera.upt@gmail.com*

Received: *10 July 2024;* ***Accepted:*** *21 January 2025;* ***Published:*** *5 August 2025.*

1. Introduction

Piezoelectric ceramics are very complex, but with specific steps, its materials are produced in a special process using specialized equipment, so the production process and equipment are not commonly known by the general public. The process includes.

a) The recipe for piezoelectric ceramics. The raw material ceramic recipe is the basis for preparing piezoelectric materials. In specific to PZT, its main raw materials are Pb_3O_4, ZrO_2 and TiO_2. The selection of raw materials should generally consider their chemical composition and physical state, normally are powders.

b) The production process for piezoelectric ceramics. The production is widely identified, mainly includes the synthesis of ceramic raw materials, molding of the part, sintering, electrode application and polarization. It produces reaction chemicals and physics modifications.

c) The equipment used to produce piezoelectric ceramics. In the process various equipment such as mixers, millers, pressing machines, grinding machines, sintering furnaces and printers are used. Some production processes may also require equipment such as automatic tape casting machines, capacitor cutting machines and water equalization presses (Admino, 2023).

The piezoelectric material which is commonly has been used in automotive and aerospace engineering nowadays there are the next: Lead Zirconate Titanate (PZT), Lead Magnesium Niobate (PMN), Sodium Potassium Niobate (SPN), Lead Titanate (LT) and Leadmetaniobate (LMN), of the five listed types of piezoelectric material above, Lead Zirconate Titanate (PZT) is one of the most frequently studied ferroelectric materials due to its vast array of applications as a pyroelectric material which is widely used for the repair of the structure, repair of cracks, shape control, vibration control and structural health monitoring (Aabid *et al*., 2021). However, PZT materials generate environmental impacts due to their manufacturing processes (Lai *et al*., 2023). Considering this reason, different piezoelectric systems are currently being studied to replace PZT materials and thus reduce the environmental impact.

The piezoelectric nanomaterials are used in systems for the energy device. Its nanomaterials produce electric current by mechanical pressure. It let charger the cell phone while walking every day, other use is the keyboard typing to supply energy to electronic systems, generate signals on a sensor in the industry or getting energy from the dancing on a floor inside of night space. Piezoelectric systems are soft and flexible today. Flexible piezoelectric nanodevices can be used to charge smart watches, phones and other smart gadgets, playing games, joints, medical applications devices, hands and feet (Shing *et al*., 2023).

The literature showed as recent development of piezoelectric actuators that transfer input electric energy into displacement, force, or movement outputs efficiently via inverse piezoelectric effect-based electromechanical coupling, on other way piezoelectric materials can convert stress changes into electrical signals that can activate different intracellular signaling pathways critical for cell activity and function (Linliang *et al*., 2023), which makes them potentially useful for nerve tissue regeneration. Other actuators as sprung up and gained widespread use in terms of compelling attributes, such as high precision, flexibility of stoke, immunity to electromagnetic interference and structural scalability. The structural scalability and load capacity make piezoelectric actuators a candidate to apply in areas of robotics, automation, industrial inspection, aerospace, automotive and defense. The development of various types of piezoelectric actuators still in study over the past decades, trying to integrate new tech or materials to improve your product's performance, so piezoelectric materials are iteratively updated, there are two types, direct actuators and indirect actuators (Zhou *et al*., 2024). The research topics and the selection of practical application are with the high electrostrain response, low hysteresis, fatigue resistance and others. The specific crystallographic orientation is an effective way of aligning anisotropic-shaped seed templates in a powder matrix using a tape casting process (Lai *et al*., 2023), so mentioned condition is necessary to the characterization with X-Ray Diffraction, with its situation got identify profiles derivate by the changes in the profile phase and this could be a cause to generate changes in the properties, on another possible ratio with the properties are the particles size obtained on nanometric ranges, in this situation the milling mix of high energy has been demonstrated that is a route to obtained particles on nanometric size, other works also studied the behavior of dopants in the structure of the ceramic system to generate a change in its final properties (Li *et al*., 2021; Tan & Wang, 2021; Blessington *et al*., 2020; Arias *et al*., 2020).

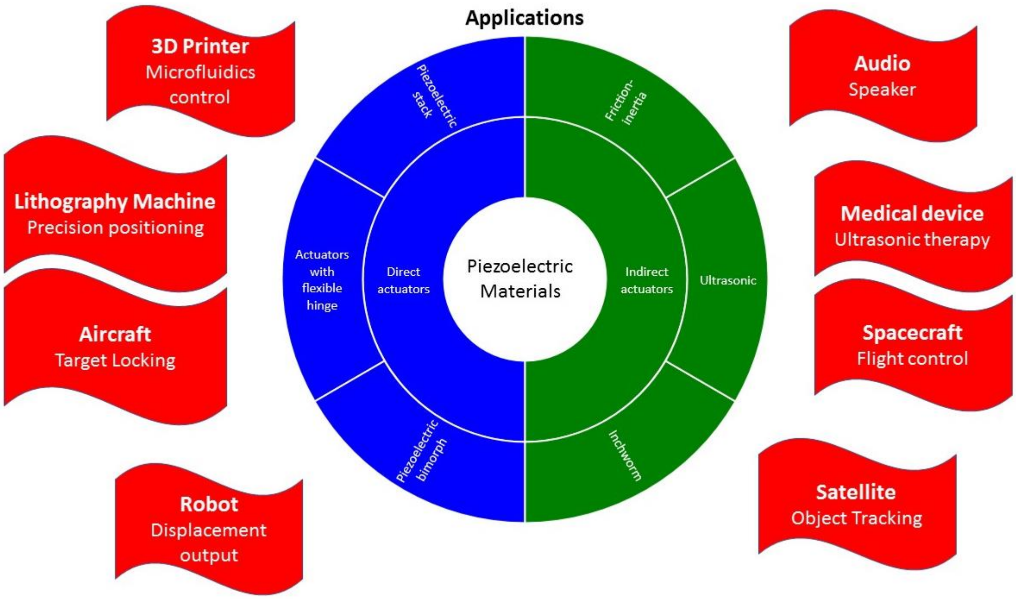

Figure 1. Piezoelectric materials applied in products

The production process of piezoelectric ceramics needs knowledge on materials science to developed better properties in materials and smaller sizes in particles in comparison with traditional engineering materials, modifications allowed achieve various applications on diverse devices, medical solutions, magnetic response, electric current, memory materials, sensors, transductors and others, is in response to current needs focused on technological advances and their uses, the study of smart materials has been accelerated on worldwide (Di Egidio *et al*., 2023; Unterlass, 2021; Estrada *et al*., 2022; Kien *et al*., 2021; García-Mendoza, 2020). Piezoelectric materials have been studied among these advanced materials. Piezoelectric materials are simple, lightweight, with low cost and easy-to-control smart material for structural actuation applications. It can easily be molded or manufactured into various forms such as patches, thin films, rectangular solids, buttons, cylinders and fibers (Aabid *et al*., 2021; Cheng *et al*., 2021). There are Piezoelectric single crystals, ceramics and polymer, the piezoelectric single crystals contain natural and synthetic materials as quartz and salt, some representative's systems are PZN-PT, PMN-PT, PIN-PT. On ceramics materials the $BaTiO_3$, AlN and piezoelectric lead zirconate titanate (PZT) with diverse applications. On the other hand, the NBT ceramic system has been studied due to the better results in dielectric and piezoelectric properties and energy storage (Aabid *et al*., 2021; Cheng *et al*., 2021; Adhikary *et al*., 2021; Chen *et al*., 2019; Ma, 2019). Today's most widely used piezoelectric material is lead-zirconate-titanate. The ceramics studied during the last time has been oriented on different ways, a particulate route is with NBT systems, so we found Nb_{5+-} doped $(Bi_{0.5}Na_{0.5})$ TiO_3 (Lai *et al*., 2023), where stoichiometric equations were applied to get grain microstructure modification, its impact on electrostrain response. The piezoelectric polymers can be further identified as bulk polymers, piezoelectric composite polymers and voided charged polymers. The typical bulk polymers are polyvinylidene fluoride (PVDF), polyamides, Parylene-C, polyimide and polyvinylidene chloride with limited applications (Zhou *et al*., 2024).

One of the best-known methods for synthesizing this type of material is the so-called "ceramic route" method, one of the basic steps of this method is the mechanical milling of the oxides and carbonate, with the technique allowing the particle size reduction; however, it can also form solid solutions, chemical reactions and crystalline phases (Pardo *et al*., 2021). Several studies have focused on the relationship between particle size and material properties and have found that smaller particle sizes improve the properties of material (Ferrero *et al*., 2022; Sun *et al*., 2021; Zhang *et al*., 2021; Yang *et al*., 2020; Li *et al*., 2020). A different synthesis is the milling of powders, also an alternative for chemical processing, performing syntheses that normally require special conditions (Ferrero *et al*., 2022; Li *et al*., 2020; Baláž, 2021). Some works have reported this method as an efficient synthesis method, obtaining complex oxides, such as the ABO_3 (Bak *et al*., 2020; Santos *et al*., 2019).

Mechanochemistry has been one of the four primary fields of chemistry during decades, alongside electrochemistry, thermochemistry and photochemistry. However, its applications still increased attention from the scientific community in recent years, owing to its numerous advantages. The advantages include the environmentally friendly nature of mechanochemical processes, in some cases there are significant reduction or complete elimination of hazardous solvents, the ability to configure the milling space under miller conditions without requiring external heat as traditional methods and the achievement of high yields in less time compared to other technologies. This has been attributed to the reduction in particle size, resulting in an increased surface area, enhanced contact between reactants, minimized mass transfer limitations and accelerated reaction rate. The mechanochemistry emerges as an indispensable method for various applications within sustainable chemistry (Arfelis *et al*., 2024).

Based on the routes of synthesis and the results obtained, the present work has been established on the synthesis, analysis, application as piezoelectric and crystalline characterization of a ceramic system NBT ($(Bi_{0.5-x}Na_{0.5+x})$ TiO_3)). The mechanosynthesis method has been selected by high-energy mechanical milling and alternative technique to get nanometric particle size, different properties and green chemical. Its method does not use acid or other materials contaminants in this process, so the process is cleaner than others.

2. Materials and methods

The powders were synthesized by the conventional oxide mixing route Bi_2O_3 (99.9 % purity, Aldrich), Na_2CO_3 (99.5 % purity, J.T. Baker) and TiO_2 (99.9 % purity FAGALAB) used as precursor reagents.

$$2TiO_2 + Na_2CO_3 + Bi_2O_3 \longrightarrow 2\ BiNaTiO_3 + CO_2 + O_2$$

The precursors were evaluated from x= 0.01 to x= 0.1 in $(Bi_{0.5-x}Na_{0.5+x})TiO_3$ with increments of 0.03, so reagents were weighed using a powder volume ratio (PVR) of 10:1. The powders were subjected to a five hours milling time in a high-energy miller (SPEX model 8000D) in stainless steel vials, steel balls. The powders were analyzed in particle size analysis equipment NanoBrook 90 plus. The powders were subjected to calcination temperate and the process was conventional slid state reaction method with add the dwell time at temperature 850 C in an air atmosphere on time for five hours, while X-Ray Diffraction analysis allowed identify the crystalline phases, using Bruker D8 equipment, with Cu *Kα1* radiation (40 kV, 40 mA), in a 2θ range from 20^o to 80^o. The crystalline phases in the ceramic were analyzed using DIFFRAC.EVA software, while the Rietveld analysis was with MAUD software to obtain the values of lattice parameters (Lutterotti *et al*., 2007). The morphology of the powders was identified using Scanning Electron Microscopy (SEM) with a JEOL equipment model JSM-IT300. The electric response of piezoelectric material was tested with an Arduino system and PLX-DAC software.

The preparation of the pill was using a mold with 1 gram of the powder and 20 tons of pressure using calcination temperate with add the dwell time at temperature 1100 C.

3. Results and discussion

3.1. X-Ray Diffraction

The results of the X-Ray Diffraction show a profile with the compositions of the material (Figure 2). The different values of x used in chemical equations allowed identify differences in profiles using patterns. On the profile with x=0.01 were observed the presence of secondary phases, while in x=0.1 and x= 0.07 was possible to determine the structures with NBT profile, so there are no identified crystalline phases secondaries in the result, was observed the more significant formation of the perovskite-type with these phase sodium bismuth titanite ($Bi_{0.5}Na_{0.5}$) TiO_3 (NBT) (COD: 2103296 R3 c: H). The green chemistry was possible using the mechanical milling of high energy.

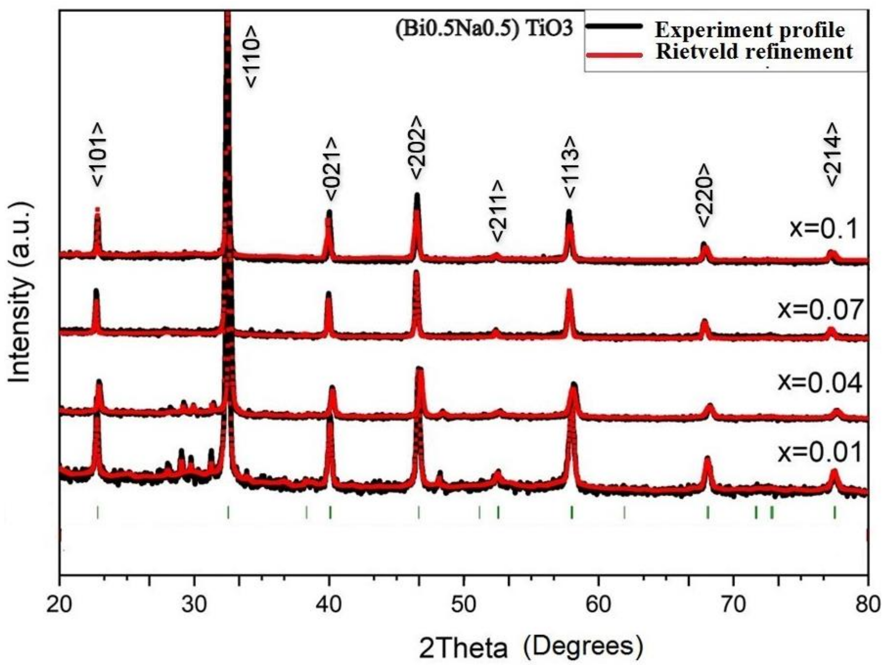

Figure 2. X-Ray Diffraction patterns for the ($Bi_{0.5-x}Na_{0.5+x}$)TiO_3

A Rietveld refinement analysis was developed, achieved the crystal size, also calculated the percentage weight phase obtained by mechanosynthesis. Table 1 shows the results of the Rietveld analysis. Note that the systems with the lowest x-value have the secondary phases Bi_2O_3 (COD: 1010311, Pn-3m: 1). At the same time, the formation of the perovskite phase is evident in all four systems, with the ($Bi_{0.5}Na_{0.5}$) TiO_3 (COD 2103295 R3c) phase and similar with the work developed by Li (2019). It could be explained by the interactions between the ions of the precursor reagents taking place to a lower order of intensity.

As for the phases with a higher value of x, these present a higher content of the $(Bi_{0.5}Na_{0.5})\ TiO_3$ phase, being the system x= 0.07 is the one that shows higher formation, so in the system x= 0.1, as for the crystal size, we can observe that both systems present a larger size than the previous two. The highest value is 6869.76 Ǻ, for the x= 0.1 system, while in the x= 0.07 system, we obtain a value of 2528.14 Ǻ. The phase of Bi_2O_3 is cubic.

Table 1. Rietveld refinement of the systems studied shows the weight percentage of each phase, the crystal size and the study's variance

Sample	Phase	µs	Lattice parameters		Cristal size Ǻ	χ^2
			a	c		
X=0.01	$(Bi_{0.5}\ Na_{0.5})\ Ti\ O_3$	11.3870 (e^{-4})	5.5014	13.5246	856.2237	1.2320
	Bi_2O_3	19.4305 (e^{-4})	5.5004	---	1179.4812	
X=0.04	$(Bi_{0.5}\ Na_{0.5})\ Ti\ O_3$	12.4447 (e^{-4})	5.4902	13.4144	596.9404	1.3681
X=0.07	$(Bi_{0.5}\ Na_{0.5})\ Ti\ O_3$	10.1923 (e^{-4})	5.5166	13.5459	2528.1487	1.2112
X=0.1	$(Bi_{0.5}\ Na_{0.5})\ Ti\ O_3$	9.917 (e^{-4})	5.4966	13.5037	6869.7646	1.8390

The $(Bi_{0.5}Na_{0.5})\ TiO_3$ ceramics crystallize in the R3c rhombohedral ferroelectric phase (Li *et al*., 2019), agreeing with the crystalline phase obtained in the XRD analysis. These rhombohedral perovskites can only present the following space groups: R3m, R3c, or R3̂c (Kumari *et al*., 2023). One of the features of the most significant interest of the part of the R3c space group is that, due to its polar symmetry, it allows the ferroelectricity of the ceramic (Gareeva *et al*., 2022). The arrangement of such unequal species in the same structure leads to a sequence of phase transitions, seen in the Rietveld analysis. The ferroelectricity, a characteristic property of NBT-based solid solutions, is attributed to the Bi^{3+} ions occupying the A sites of the perovskite structure (Roukos *et al*., 2019).

3.2. Particle size analysis

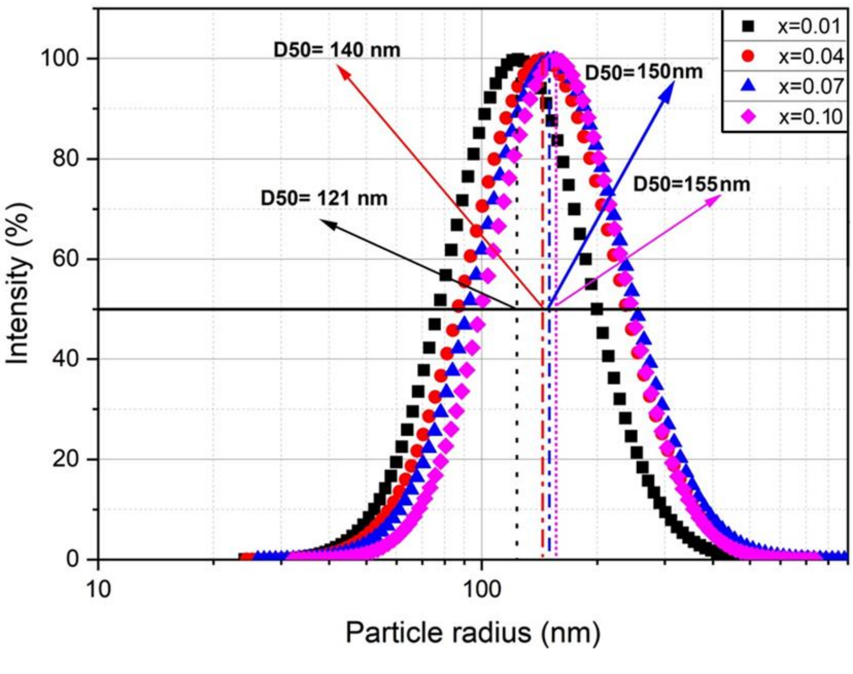

Figure 3. Particle size distribution of the four systems analyzed

The particle size analysis results of the four systems studied are presented in Figure 3. The difference in the size of the systems is marked when the content of Bi^{3+} and Na^{2+} ions varies. For example, when the system is x= 0.01 and 0.04, the ceramics present the smallest size, observing particle radius sizes around 120 and 140 nm. In contrast, the compositions with higher x values show average sizes between 150 and 155 nm.

3.3. Morphology

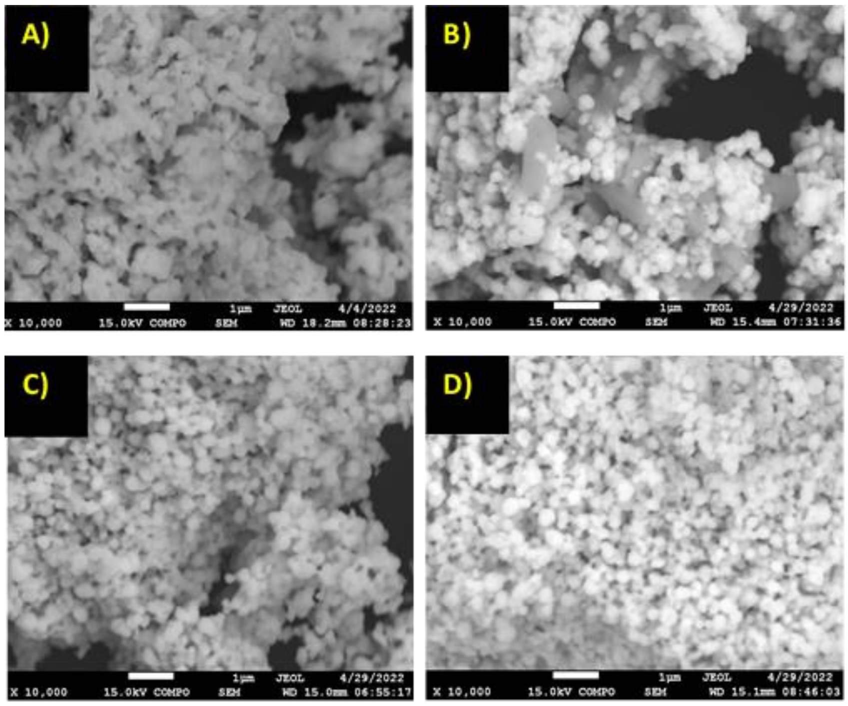

Figure 4. Photographs of the analyzed ceramic systems. A) system x=0.01 NBT; B) system x=0.04; C) system x= 0.07; D) system x= 0.1

The results of the morphology of the ceramic material using a Scan Electron Microscope are shown in Figure 4. We can see that most of the systems present a marked distribution of particle sizes, mainly in the form of particle agglomerates. In terms of the morphology of the particles, the larger ones tend to have sub-euhedral shapes, while the smaller ones do not have regular.

3.4. Results as piezoelectric

The powders were compacted in pill form (Figure 5), so during the experiments on diverse testers with various grams in weight, the results showed that the best of the results was using 1 gram of powders under a load of 20 tons, it generated pills without fissures, the temperature applied was on 1100°C allowed got pill with dimensions of 16 millimeters diameter and 1.2 millimeters in thickness.

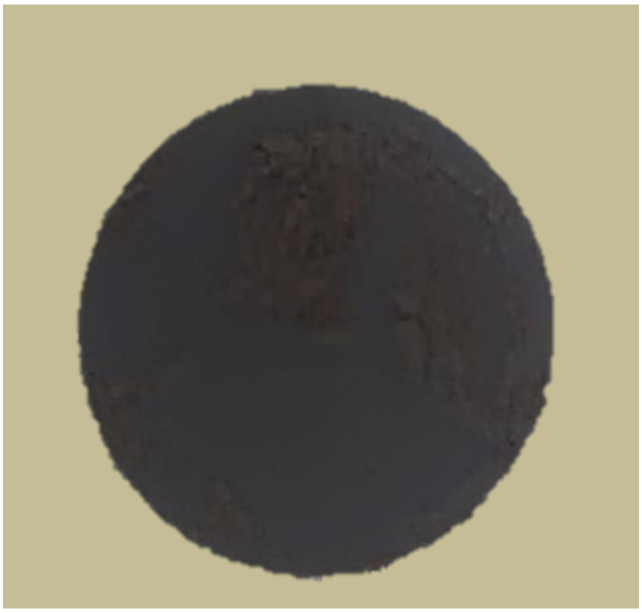

Figure 5. NBT in pill form

The pill material was used to mount in a device (Figure 6) to evaluate the response when the material was subjected to pressure, on that moment registered the electrical response, the measurement allowed the validation of piezoelectric properties, a silver paste was used on the pill and was applied a bath of silicone to reorient electronic dominium and generate voltage.

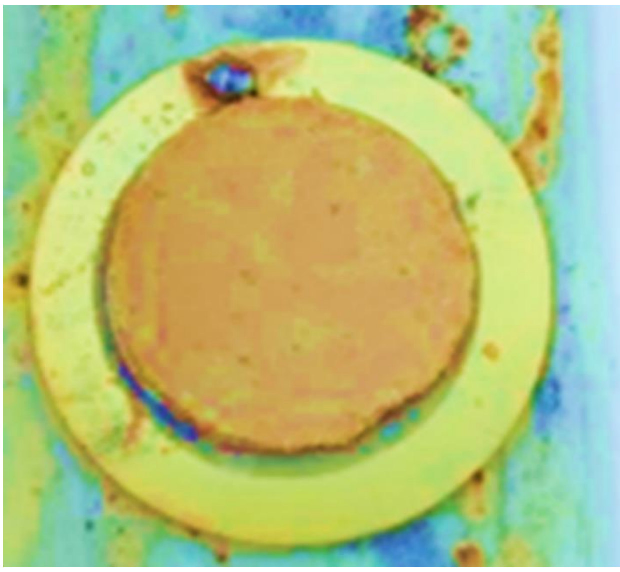

Figure 6. Device to evaluate the electric response

The results using the device and software PLX-DAQ allowed observe the electric response when was applied a pressure as is shown in Figure 7, the voltage reaches values of 5 V, the result is higher than the 3 volts obtained by Mwanzia Bonface and Paul Kamweru on 2020 (Bonface & Kuria, 2020).

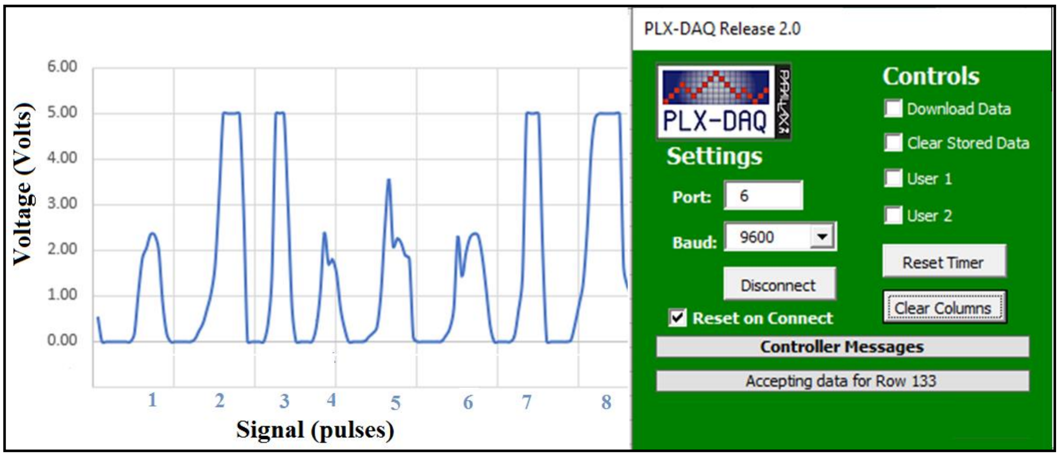

Figure 7. Results of voltage using the device with material NBT

4. Conclusions

A piezoelectric pill lead-free was develop using a green chemistry, the results showed that high-energy mechanical milling at a time of 5 h, accompanied by calcination temperate and the process was conventional solid state reaction method with add the dwell time at temperature 850 C, it was an efficient process to obtain piezoelectric ceramics with structure $(Bi_{0.5}Na_{0.5})TiO_3$. Based on these results, we can confirm that high-energy mechanical milling is an effective process for obtaining complex ceramic powders with irregular morphology, nanometric size and piezoelectric parts with voltage of 5V tested with Arduino, it is a route to develop advanced ceramics materials with applications to energy. The synthesis times are lower than other methods reported.

Acknowledgment

This project was carried out thanks to the support of the Consejo Mexiquense de Ciencia y Tecnología through the program “Specialized Research Stays”.

References

Aabid, A., Raheman, M.A., Ibrahim, Y.E., Anjum, A., Hrairi, M., Parveez, B., ... & Mohammed Zayan, J. (2021). A systematic review of piezoelectric materials and energy harvesters for industrial applications. *Sensors*, *21*(12), 4145. https://doi.org/10.3390/s21124145

Admino, H. (2023). How are piezoelectric ceramics made? Heshuai. https://www.he-shuai.com/how-are-piezoelectric-ceramics-made/

Arfelis, S., Martín-Perales, A.I., Nguyen, R., Pérez, A., Cherubin, I., Len, C., Malpartida, I., … & Fullana-I-Palmer, P. (2024). Linking mechanochemistry with the green chemistry principles: Review article. *Heliyon*, *10*(14), e34655. https://doi.org/10.1016/j.heliyon.2024.e34655

Arias, N.P., Giraldo, O.H., Gómez, E.S., González, B.E., González-Moran, Carlos O., Hernández, J.G. & Flores-Cuautle, J.D.J.A. (2020). Electrical response in poled $(Bi_{0.5}Na_{0.5})_{0.935}Ba_{0.065}TiO_3$ ceramics. *Ferroelectrics*, *558*(1), 67-78. https://doi.org/10.1080/00150193.2020.1738183

Bąk, W., Dulian, P., Garbarz-Glos, B., Czekaj, D. & Lisińska-Czekaj, A. (2020). Alternative, direct synthesis method of the ceramic solid solutions based on $BaTiO_3$ through a high energy ball milling. *Archives of Metallurgy and Materials*, *65*(2020), 805-810. http://doi.org/10.24425/amm.2020.132824

Baláž, M., (2021). *Environmental Mechanochemistry: Recycling Waste into Materials Using High-Energy Ball Milling*. Springer-Nature. https://doi.org/10.1007/978-3-030-75224-8

Blessington, A.P., Suriakarthick R., Aravinth, K., Murugaraj, R. & Venkateswaran C. (2020). Optical and electrical behavior of pristine and Mn doped 0.935($Bi_{0.5}Na_{0.5}TiO_3$)-0.065 $BaTiO_3$ lead free piezoelectric ceramics. *AIP Conference Proceedings*, 030458. https://doi.org/10.1063/5.0017682

Bonface, M., Kuria, K.P. (2020). Generating, rectifying and stepping up the voltage output of piezoelectric plate. *Generating, Rectifying and Stepping up the Voltage Output of Piezoelectric Plate*, *56*(1), 8.

Chen, P., Yang, C., Cai, J., Wang, Z., Zhang, L., Shi, W. & Yu, K., (2019). Effect of bismuth excess on the energy storage performance of 0.5 $Na_{0.5}Bi_{0.5}TiO_{3-0.5}$ $SrTiO_3$ ceramic. *Materials Research Express*, *6*(12), 126306. https://doi.org/10.1088/2053-1591/ab56f1

Cheng, Y., Xing, J., Wang, T., Wang, F., Li, R., Sun, X. & Zhu, J., (2021). Realization of densified microstructure and large piezoelectricity in KNN ceramics via the addition of oxide additives. *Journal of Materials Science: Materials in Electronics, 32*(15), 20211-20224. https://doi.org/10.1007/s10854-021-06525-x

Das Adhikary, G., Sharma, D., Punetha, P., Jafo, G., Abebe, G., Mishra, A., ... & Ranjan, R. (2021). Preponderant influence of disordered P4bm phase on the piezoelectricity of critical compositions of $Na_{0.5}Bi_{0.5}TiO_3$-based ferroelectrics. *Physical Review B*, *104*(18), 184102. https://doi.org/10.1103/PhysRevB.104.184102

Di Egidio G., Martini, C., Ceschini, L. & Morri, A. (2023). Influence of electroless nickel-DLC (diamond-like carbon) multilayer coating on the mechanical performance of the heat-treated $AlSi_{10}Mg$ alloy produced by powder bed fusion-laser beam. *Materials*, *16*(9), 3313. https://doi.org/10.3390/ma16093313

Estrada, S.A., Guger I., Febbraro, J., Turak, A., Lin, H.R., Salinas Y. & Brüggemann O. (2022). Synthesis and spatial order characterization of controlled silica particle sizes organized as photonic crystals arrays. *Materials*, *15*(17), 5864. https://doi.org/10.3390/ma15175864

Ferrero, G., Astafiev, K., Ringgaard, E., de Oliveira, L.S., Sudireddy, B.R., Haugen, A.B., ... & Rojac, T. (2023). Piezoelectric properties of mechanochemically processed 0.67$BiFeO_3$-$_{0.33}BaTiO_3$ ceramics. *Journal of the European Ceramic Society*, *43*(2), 350-361. https://doi.org/10.1016/j.jeurceramsoc.2022.10.024

Garcia-Mendoza, T., Martinez-Garcia, A., Becerril-Juarez, I.G., Lopez-Vazquez, E., Avalos-Borja, M., Valera-Zaragoza, M. & Juarez-Arellano, E.A., (2020). Mechanosynthesis of metastable cubic δ-$Ta_{1-x}N$. *Ceramics International*, *46*(14), 23049-23058. https://doi.org/10.1016/j.ceramint.2020.06.082

Gareeva, Z., Zvezdin, A., Zvezdin, K. & Chen, X. (2022). Symmetry analysis of magnetoelectric effects in perovskite-based multiferroics. *Materials*, *15*(2), 574. https://doi.org/10.3390/ma15020574

Kumari, S., Anand, K., Alam, M., Ghosh, L., Dixit, S., Singh, R., ... & Chatterjee, S. (2023). Enhancement of multiferroic and optical properties in $BiFeO_3$ due to different exchange interactions between transition and rare earth ions. *Physica Status Solidi (b)*, *260*(9), 2300026. https://doi.org/10.1002/pssb.202300026

Lai, L., Zhao, Z., Tian, S., Ou, B., Liang, G., Li, B. & Dai, Y. (2023). Ultrahigh electrostrain with excellent fatigue resistance in textured Nb_{5+}-doped ($Bi_{0.5}$Na0.5)TiO_3-based piezoceramics. *Journal of Advanced Ceramics*, *12*(3), 487-497. https://doi.org/10.26599/JAC.2023.9220698

Li, C., Zhang, M., Ruan, M., Wang, J., Liang, J. & Zhang, D. (2020). A nanograins-attached and ultrathin Cu flake powder fabricated by high energy mechanical milling and dealloying. *Materials Letters*, 265, 127432. https://doi.org/10.1016/j.matlet.2020.127432

Li, Q., Wang, C., Zhang, W. & Fan, H. (2019). Influence of compositional ratio K/Na on structure and piezoelectric properties in [($Na_{1-x}K_x$)*0.5*$Bi_{0.5}$]$Ti_{0.985}Ta_{0.015}O_3$ ceramics. *Journal of Materials Science*, 54, 4523-4531. https://doi.org/10.1007/s10853-018-3174-7

Li, Y., Borbely, M. & Bell, A. (2021). The influence of oxygen vacancies on piezoelectricity in samarium-doped Pb ($Mg_{1/3}Nb_{2/3}$) O_3-$PbTiO_3$ ceramics. *Journal of the American Ceramic Society*, *104*(6), 2678-2688. https://doi.org/10.1111/jace.17619

Lutterotti, L., Bortolotti, M., Ischia, G., Lonardelli, I. & Wenk, H.R. (2007). Rietveld texture analysis from diffraction images. *Zeitschrift fur Kristallographie, Supplement*, 26, 125-130. https://doi.org/10.1524/9783486992540-020

Ma, W., Fan, P., Salamon, D., Kongparakul, S., Samart, C., Zhang, T., ... & Zhang, H. (2019). Fine-grained BNT-based lead-free composite ceramics with high energy-storage density. *Ceramics International*, *45*(16), 19895-19901. https://doi.org/10.1016/j.ceramint.2019.06.245

Nguyen, K., Bellec, E., Zatterin, E., Le Rhun, G., Gergaud, P. & Vaxelaire, N. (2021). Structural insights of electrical aging in PZT thin films as revealed by in situ biasing X-ray diffraction. *Materials*, *14*(16), 4500. https://doi.org/10.3390/ma14164500

Pardo, L., García, Á., Schubert, F., Kynast, A., Scholehwar, T., Jacas, A. & Bartolomé, J.F. (2021). Determination of the PIC700 ceramic's complex piezo-dielectric and elastic matrices from manageable aspect ratio resonators. *Materials*, *14*(15), 4076. https://doi.org/10.3390/ma14154076

Roukos, R., Romanos, J., Abou Dargham, S. & Chaumont, D. (2019). Quantification of relaxor behavior in (1−x) $Na_{0.5}Bi_{0.5}TiO_{3-x}CaTiO_3$ lead-free ceramics system. *Journal of the European Ceramic Society*, *39*(7), 2297-2303. https://doi.org/10.1016/j.jeurceramsoc.2019.02.015

Santos, A.G., Leite, J.O., Gimenez, I.F., Souza, M.J.B. & Pedrosa, A.G. (2019). Effect of the B-site cation from $LaBO_3$ and $LaBO_3/TiO_2$ (B=Mn or Ni) perovskites prepared by mechanosynthesis in adsorption of Congo red dye from aqueous medium. *Materials Research Express*, *6*(10), 105065. https://doi.org/10.1088/2053-1591/ab3b22

Singh, P., Kaur, G., Shandilya, M., Rana, P., Rai, R., Mishra, Y., Syväjärvi, M. & Tiwari, A. (2023). Trends in piezoelectric nanomaterials towards green energy scavenging nanodevices. *Materials Today Sustainability*, 24, 100583. https://doi.org/10.1016/j.mtsust.2023.100583

Sun, S., Liu, H., Fan, L., Ren, Y., Xing, X. & Chen, J. (2021). Structural origin of size effect on piezoelectric performance of Pb (Zr, Ti) O_3. *Ceramics International*, *47*(4), 5256-5264. https://doi.org/10.1016/j.ceramint.2020.10.106

Tan, L., Wang, Y. (2021). Phase evolution and associated electrical properties of Al-doped KNN–$Bi_{0.5}Na_{0.5}ZrO_3$ lead-free piezoelectric ceramics. *Journal of Physics and Chemistry of Solids*, 151, 109797. https://doi.org/10.1016/j.jpcs.2020.109797

Unterlass, M.M. (2021). Recent advances in hydrothermal materials synthesis. *Journal of Materials Chemistry A*, *9*(2), 661-662, http://dx.doi.org/10.1039/D0TA90284E

Wang, N., Tang, Y., Pan, W. & Zhang, B. (2020). Enhanced electrical properties of lead-free $(Ba_{1-x}Ca_x)(Ti_{0.94}Zr_{0.01}Sn_{0.05})O_3$ piezoelectric ceramics by optimizing phase ratio and sintering temperature. *Journal of Materials Science: Materials in Electronics*, *31*(23), 21682-21692. https://doi.org/10.1007/s10854-020-04681-0

Yang, P., Peng, W., Xu, K., Li, L. & Yu, S. (2021). Effect of the particle diameters of raw materials on the structure, micromorphology, dielectric and tunable performance of $(Ba_{0.91}Ca_{0.09})(Zr_{0.2}Ti_{0.8})O_3$ ceramics. *Ceramics International*, *47*(7), 8930-8935. https://doi.org/10.1016/j.ceramint.2020.12.013

Zhang, R., Li, L., Long, S., Shen, Y., Lou, H., Wen, F., ... & Wu, W. (2021). Linear and ferroelectric effects of $BaTiO_3$ particle size on the energy storage performance of composite films with different polymer matrices. *Ceramics International*, *47*(15), 22155-22163. https://doi.org/10.1016/j.ceramint.2021.04.238

Zhou, X., Wu, S., Wang, X., Wang, Z., Zhu, Q., Sun, J., ... & Lu, Q. (2024). Review on piezoelectric actuators: Materials, classifications, applications and recent trends. *Frontiers of Mechanical Engineering*, *19*(1), 6. https://doi.org/10.1007/s11465-023-0772-0