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Research Article

A PLZT Novel Sensor with Pt Implanted for Biomedical Application: Cardiac Micropulses Detection on Human Skin

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Advances in sensors for biomedical applications have been a great motivation. In this research, a PLZT (lead lanthanum zirconate titanate) novel sensor with platinum wire implanted in its longitudinal section was developed through of the synthesis process based on powder technology. The raw materials as lead (PbO), lanthanum (La_2O_3), zircon (ZrO_2), and titanium (TiO_2) were used in the formation of the chemical composition (62.8% PbO, 4.5% La_2O_3, 24.2% ZrO_2, and 8.5% TiO_2). Then, these powders were submitted to mix-mechanical milling at high energy; cylindrical samples with the implant of the platinum wire were obtained with the load application. Finally, the compacted samples were sintered at 1200°C for 2 hours, then followed by a polarization potential of 1500 V/mm at 60°C to obtain a novel sensor. The density and porosity were evaluated using the Archimedes' principle, while the mechanical properties such as fracture toughness value and Young's modulus were determined by indentation and ultrasonic methods, respectively. A microscopic examination was also carried out to investigate the structural properties of the material. The PLZT novel sensor is electronically arranged for monitoring the cardiac pulses through a data acquisition system. The results obtained in this research are analyzed and discussed.

1. Introduction

Since the discovery of ceramic ferroelectric materials in 1940, lead and titanates perovskites had been of great interest due to their dielectric and piezoelectric properties [1]. Nowadays several researches are in search of better materials and manufacturing processes for the development of piezoelectric materials considering lead-zirconate-titanate relationship (PZT). In this sense, systems such as PZT-SKN and PZT-SNN have been studied to find excellent dielectric, piezoelectric, and moisture resistance properties [2]. Another ferroelectric material investigated is a quaternary system based on lead lanthanum zirconate titanate known as PLZT [3, 4], where the effects of sintering temperature on the electrical properties are reported elsewhere, considering the manufacturing process by mechanical alloying technique. Other research approaches of interest are the thermophysical, electrical fatigue, and photovoltaic properties [3, 5, 6]. In the continuous search for new ferroelectric materials, efforts have been made in research which focuses on lead-free systems as suitable materials for biomedical applications, as in the case of barium titanate ($BaTiO_3$) and its derivatives (Na,Bi)Ti-$BaTiO_3$-(K,Bi)TiO_3 (BNBK) and (K,Na)NbO_3 (KNN) [7, 8]. In general, these materials have a variety of applications due to good piezoelectric and dielectric properties in several applications such as optical, thermal gas, and moisture sensors as capacitors and for piezoelectric transducers [9–11]. Since the mechanical and microstructural behavior of a PLZT sensor with platinum wire implanted (PLZT-Pt) is a key factor in biosensor applications, its viability for monitoring the cardiac pulse on skin is studied in this research. Regarding this type of ceramic sensors there is no information reported in the literature about sensors manufactured by using identical or similar materials; the only work that has been reported previously is results from the same research group; then, in this research, a detailed study on the microstructural behavior is added to the previous information, and the scarce information on this sensor makes the PLZT-Pt an attractive material for biosensors application in the medical industry [12–14]. Therefore, it is possible to take PLZT-Pt measurements from different locations of the body, for example, forehead, forearm, knee, and neck.

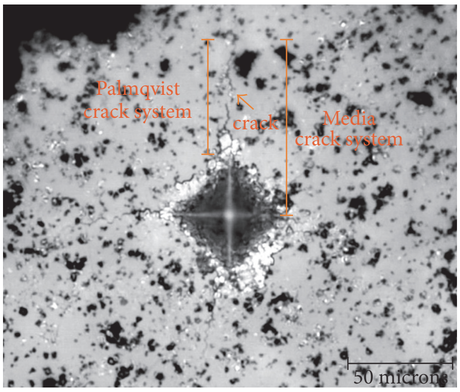


Figure 1: Vicker hardness test using a load of 1.96 N on ferroelectric ceramic materials.

2. Experimental Procedure

2.1. Sample Preparation. PLZT ferroelectric ceramics were manufactured from various oxide fine powders used as raw materials. Lead, lanthanum, zirconium, and titanium oxides all 99.9% purity were used. Considering the chemical equation of $Pb_{1-x}La_x(Zr_{1-y}Ti_y)_{1-x/4}O_3$ generally known as (9/65/35), the oxides used as raw powder material were mixed in appropriate proportions. The previously mixed oxides were then milled in an automatic mill cylinder (Pulverisette 2, Fritsch); polyvinyl alcohol was used as binder to provide a uniform milling mix. The milled mixture was cold pressed using a 35 MPa of uniaxial pressure to produce cylindrical compacts of 10 mm diameter and 3 mm thickness; this product is known as green compact.

The green compacts obtained were heat treated at 800°C in air atmosphere furnace for half hour and then grinded again. During cold forming a platinum wire (300 μm diameter) was placed in the middle of the cylinder; this one is parallel to the transversal section of the cylinder. The annealed powder was uniaxially compacted and then sintered at a heating rate of 5°C/min to rise to 600°C; this temperature was kept constant for one hour, and then the temperature was further increased to 1200°C at 10°C/min; this temperature was also maintained constant for one hour.

This heat treatment named sintering was carried out in a graphite crucible at laboratory conditions. The sintered PLZT samples were polished to prepare electrodes, in which a silver ink was applied to increase the electrical conductivity on the electrodes. A polarization test was performed using an electric field of 1.5 kV for one hour under silicone oil.

2.2. Material Characterization. Once the PLZT electrodes were manufacture by mechanical milling processing, the physical, mechanical, and electrical properties were then evaluated as follows: density and open porosity were determined using Archimedes principle.

Indentation test was used to evaluate the hardness and fracture toughness of the samples using a Vickers indenter (EMCO-TEST). The fracture toughness K_{ic} was determined using several theoretical and empirical mathematical models that can be found elsewhere [15–17]. These mathematical models consider Young's modulus and the fracture mechanisms per Palmqvist Crack System (PCS) and the Media Crack System (MCS). The difference between the both systems is the reference point used to measure crack length; that is, PCS model considers the size of the crack from the apex of the mark made by the Vickers indenter to the end point of the crack and, in the case of MCS model, this one considers the size of the crack measured from the middle footprint indenter to the end point of the crack [16]. Figure 1 shows the PCS and MCS models to determine the hardness and fracture toughness values, respectively.

An optical microscope was used to determine the microstructural features by using an inverted metallurgical microscope (MO-OLYMPUS, GX51), while the piezoelectric characterization was conducted using a homemade mechanism. This setup consists of constant weight pulse (gram-force) at a frequency of 2.26 Hz over the CCP in the same zones such as optical setup. The components of this setup were on a 24 V CD control motor Micro Switch 33VM82-020-11. The CCP has struck in a pulsed manner by a controlled mechanism developed in our laboratory; the experimental setup is described in Figure 2.

The force applied was 53.9 mN and signals were record in a SRS-Low Current Noise Preamplifier. Those records were registered by an Agilent oscilloscope measuring their peak to peak voltage to construct its graphics in which the Z-axis is the magnitude of the photovoltaic current of each record.

A continuous and controlled force was applied to produce at constant rate in the mechanism. This mechanism hit the ceramic in a specific zone; therefore, it is possible to test different points on the ceramic surface; in this research three different points were tested as shown in Figure 3.

The experimental setup used to get the patient's cardiac pulses was as follows: he was placed in a horizontal position and, for recording the electrical activity of his heart, the electrocardiographic (ECG) electrodes were placed on the lead I and the PLZT sensor was placed on the index finger of the patients' left arm, as shown in Figure 4, to measure the blood flow that results from the pulsations of blood occurring with each heartbeat. The ECG and PLZT-Pt sensor signals were registered and their peak to peak voltage was measured.

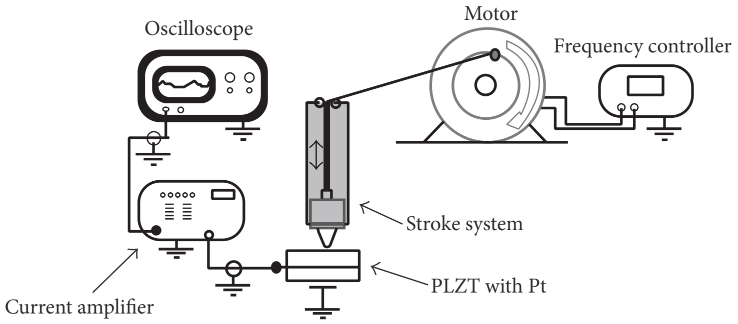


Figure 2: System to determine mechanical characterization on PLZT ceramic with Pt.

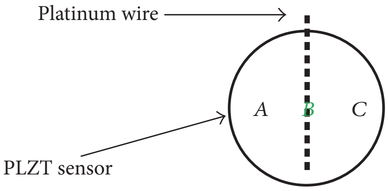


Figure 3: *A*, *B*, and *C* records acquired.

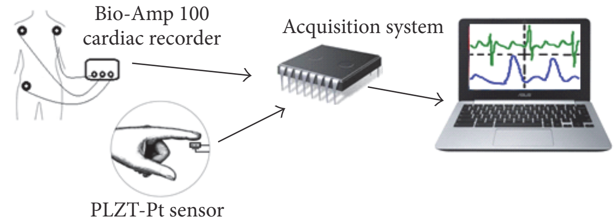


Figure 5: Diagram arrangement of data acquisition system for recording ECG data and cardiac pulses.

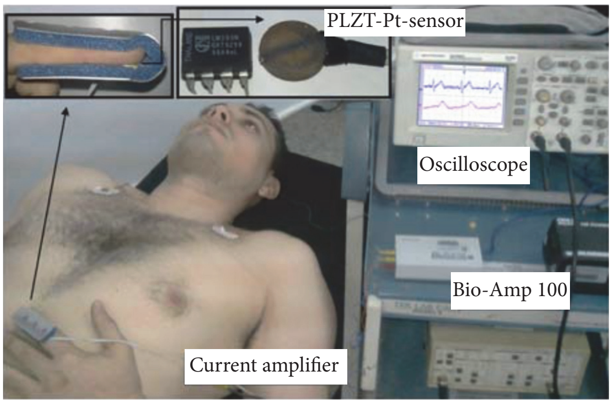


Figure 4: First experimental setup of the obtained micropulsations from PLZT-Pt sensor.

After first experimental setup using and oscilloscope as cardiac monitor, piezoelectric signal was now monitored using a low current amplifier (SRS-Low Current Noise Preamplifier SR570) and data acquisition system NI USB-6000 (600 samples per second and 8 bits of resolution) as shown in Figure 5. PLZT sensor was then placed on the index finger using a finger splint and it recorded the mechanical heart pulses in a piezoelectric manner.

2.3. Signals Recording. Electrocardiographic signals were obtained using lead I configuration and an instrumentation amplifier (Bio-Amp 100); a PLZT sensor and low current amplifier were used to get pulse signal from the index finger. MATLAB program was used to process the obtained signals. Figure 6 shows a screenshot of this program.

3. Results and Discussion

The results obtained by the Archimedes principle establish a relationship between the mass and volume of the materials after being hot sintered in the solid state. All the manufacture ceramics resulted in densities near 7.72 g/cm^3, without neglecting the mass of Pt implant (0.0061 g), which represents about 96% of the theoretical density (8.03 g/cm^3), while certain open porosity of about 3% was found on those ceramic materials. The good densification achieved in the ceramics is directly related to the sintering process conditions; this is because the material is consolidated by the diffusion interactions in the solid state, which also relates to the density and porosity that were found in the material.

The preheating ramps in the sintering cycle have microphysical effects on the homogenization temperature that activate the diffusion mechanisms and consequently establish the microstructural and morphological features of the material to achieve the desired ferroelectric properties. Not only mass transport phenomena and structural morphology are affected but also the mechanical properties of hardness, fracture toughness and Young's modulus. The characteristic mechanical behavior of these variables in ceramic materials is well known; it is known that hardness and elasticity modulus for ceramics typically have large values, while the fracture toughness is relatively low; the fact that these materials are brittle and sensitive causes a mechanical fracture when

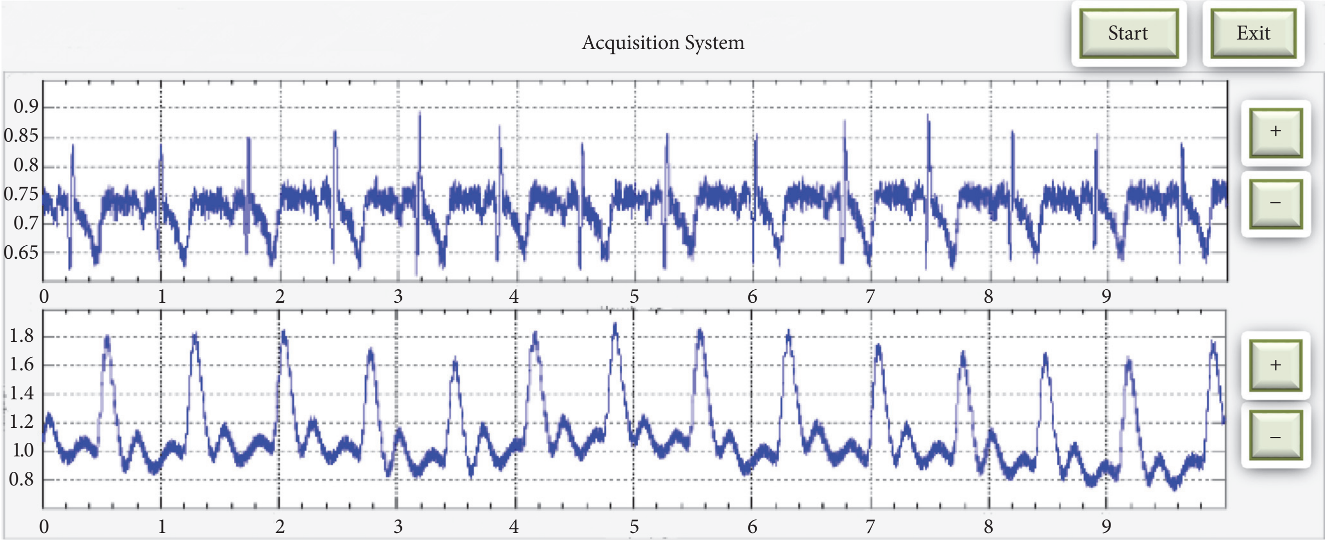


Figure 6: Electrocardiographic spectra that register the cardiac pulse and ECG signal obtained by using the sensor PLZT with Pt wire implanted.

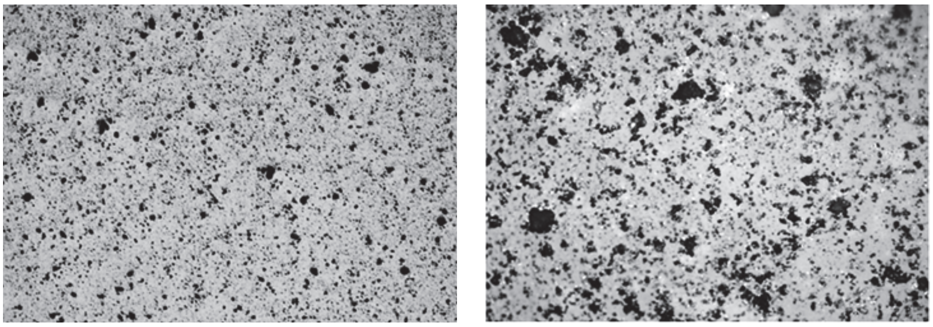

(a) (b)

Figure 7: Optical microstructure images of ferroelectric ceramics, obtained at 10x and 100x, (a) and (b) respectively.

subjected to mechanical stress as tension, compression, and impact. Under this consideration it is important to know the value of these parameters on the PLZT material manufactured due to the handling, and the results of Table 1 indicate that the material has a hardness value of 5.2 GPa with a deviation of 0.9, while the elastic modulus measured was 125 GPa with a deviation of 2, measured from the relation $\mu = \rho * \varepsilon^2$ where, μ is the elastic modulus, ρ is the experimental specific density in the material, and ε is the measured speed sound in the material. Table 1 shows the results of the ceramic tenacity to fracture determined by the models used; there is an increase ranging from the lowest value (0.68 ± MPa $\sqrt{\text{m}}$) obtained through Charles Evans model to the highest determined model Niihara with a value of 1.10 ± 0.17 in the MCS. For the case of K_{ic} measured by PCS system Lawn model with a value of 0.51 ± 0.08 was determined and the highest value was 0.87 ± 0.17 using Niihara model. The variation of this mechanical parameter regarding models allows a comparative value, considering that the values of the fracture toughness are low, and indicates that the material is susceptible to failure by mechanical stress. In this sense, there are mathematical models based on computing to describe the fracture mechanisms by indentation method to determine K_{ic} parameter, which considers the variation of the models that have been used for the determination of this mechanical variable [18].

The microstructure of the ferroelectric material was obtained using optical microscopy technique as shown in Figure 7. The images of the microstructure were taken at various magnifications to show the porosity in the material as shown in Figures 7(a) and 7(b) taken at 10x and 100x, respectively. The light gray phase corresponds to the consolidated ceramic matrix and the second phase in black color corresponds to the porosity, which is clearly identified as pores, most of them with circular or irregular morphology. Porosity is an important indicator in the material densification; namely, if the sintering temperature is greater the porosity decreases and the mechanical behavior of the material

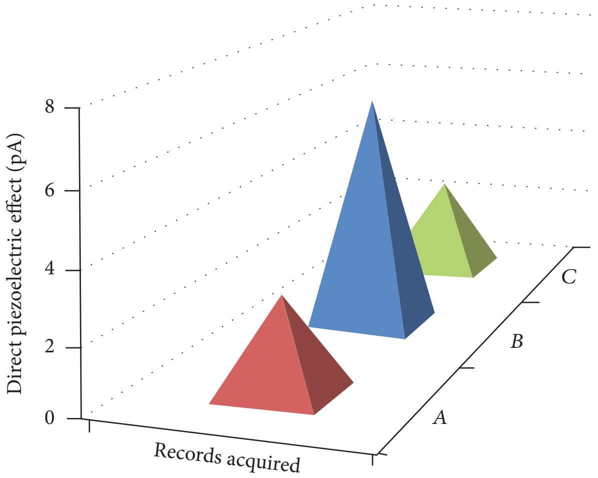


Figure 8: Piezoelectric response of PLZT ceramic with Pt implant.

Table 1: Hardness, Young's modulus, and fracture toughness of ferroelectric ceramics.

Hardness (HV/GPa)	Young's modulus (μ/GPa)	Fracture toughness (K_{ic}/Mpa$\sqrt{}$m)	
		Model	*Media crack system*
		Evans-Charles	0.68 ± 0.10
		Lawn	0.72 ± 0.11
		Lawn-Evans	0.75 ± 0.11
5.2 ± 0.9	125 ± 2	Antis-Lawn	0.78 ± 0.12
		JIS*	0.88 ± 0.13
		Niihara	1.10 ± 0.17
		Model	*Palmqvist crack system*
		Lawn	0.51 ± 0.08
		Niihara	0.87 ± 0.17

*JIS: Japanese industrial standard.

directly affects its elastic modulus and fracture toughness. The sintering temperature affects not only the physical and mechanical properties but also the ferroelectric behavior as porosity directly affects the dielectric properties considering that the air lodged in the porosity affects dielectric permeability; that is, higher porosity involves lower dielectric coefficient and vice versa; low porosity increases the dielectric coefficient [19]. Although the aim of this study is not to analyze the effect of porosity in the electrical properties of PLZT materials, it is important to note that the porosity and shape are important factors in the manufacture of ferroelectric materials due to their application as biological sensors [9].

The piezoelectric effect was evaluated on selected areas of the ceramic in Figure 3; the magnitude of the pulse generated measured in each zone was different as shown in Figure 8; however a significant result is observed in region *B*; this region is on top on the implant of platinum, where the averaged pulse response obtained was 42.26% larger than areas *A* and *C*. These changes in amplitude of measured pulse indicate that the material is more sensitive due to the platinum implant.

On the other hand, Figures 9 and 10 show the recorded ECG spectra and heart rate in effortless and effort conditions, respectively, in addition to its frequency spectrum obtained by Fast Fourier Transform (FFT). For comparison purposes, recorded in vivo signal spectra were obtained from a healthy patient of 32 years old. In general, this pulse signal (acquired from PLZT-Pt ceramic) shows a phase shift when it is compared with ECG signal in the record time (s). Pulse signal obtained by our developed sensor has similarity to the signals obtained from the aortic pressure obtained optically by the photoplethysmograph as well; main pulse signal frequency was 1.4 Hz effortlessly and 1.56 Hz with effort. In the frequency spectra, several similar frequencies can be seen; however the magnitude of the effort signal is 50% higher due to increasing the micropulse in the fingertip.

The responses of the micropulses are important because they are the signal of the operation of the PLZT-Pt ceramic sensor and its a possible medical application leaving base of the operation thereof as a novel sensor with various other applications [12]. In contrast, PLZT-Pt sensor is capable only of measuring heart rate (HR), and less reliably than with ECG electrodes. The key challenges with PLZT technology are cancelling the effects of ambient light, accommodating different skin conditions and colors, and dealing with physical motion artifacts. Additionally, PLZT sensor can only be used on parts of the body that have a high concentration of blood vessels [20].

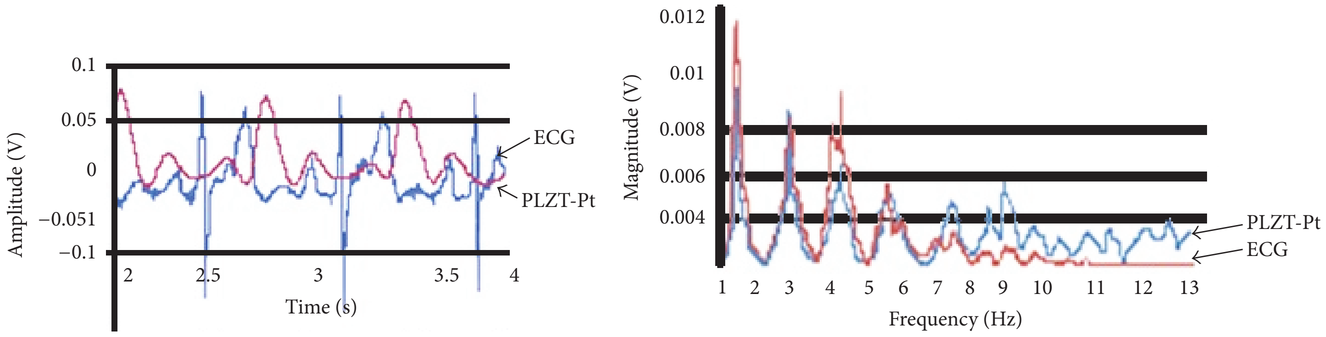
4. Conclusions

By using solid state reaction technique, it is possible to make advanced PLZT ferroelectric ceramics with platinum wire implanted considering that platinum implant supports sintering temperature conditions due to its high melting point. Ceramic reaches about 96% of theoretical densification ensuring consolidation of the material; obtained porosity near 3% does not affect ferroelectric properties obtaining a novel sensor with platinum implant.

Measured mechanical properties are characteristic of ceramic materials, considering this material as fragile in handling due to its high hardness and low fracture toughness.

The implementation of a system for monitoring blood vessels pulses enables obtaining heartbeat from different body parts; this is important for the diagnosis of possible blood vessels obstructions; on the other hand, this system is portable by using a signal conditioning and a display to work in different environments. In addition, using this system, it is possible to analyze heart rate variability without using the ECG because you can work with the maximum pulse peak as reference.

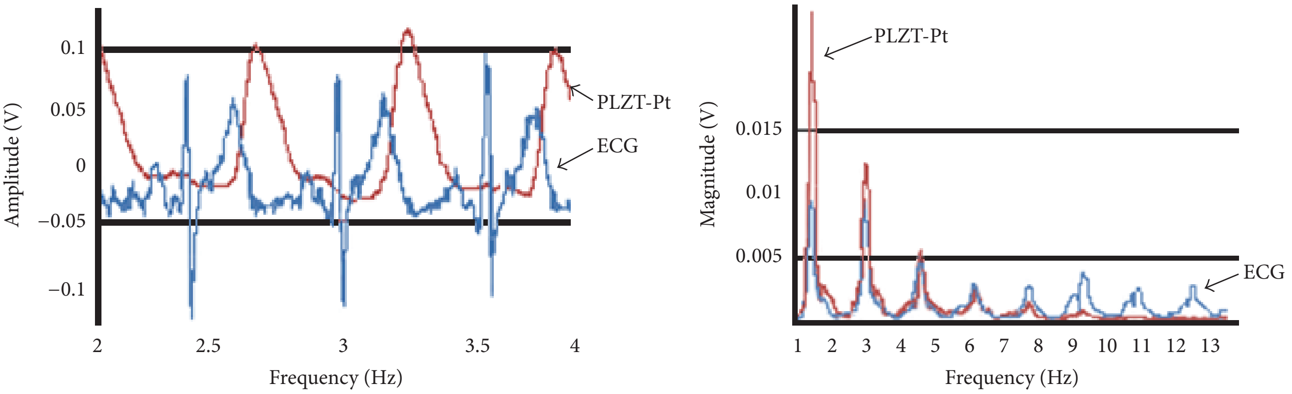
The PLZT ceramic implant has several applications in biomedical engineering and physics as it can capture various phenomena such as acoustic, mechanical, electrical, and optical [7].



(a)

(b)

Figure 9: (a) ECG signal register and cardiac pulses monitor in effortless condition and (b) frequency spectrum recorded without effort condition.



(a)

(b)

Figure 10: (a) ECG signal register and cardiac pulses monitor in effort condition and (b) frequency spectrum recorded with effort condition.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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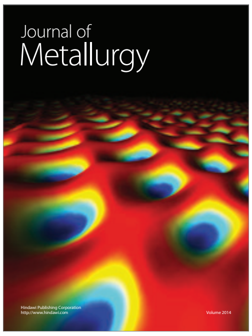
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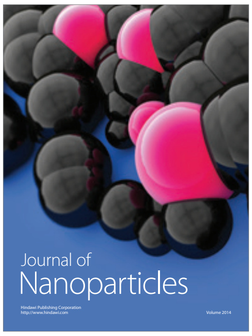
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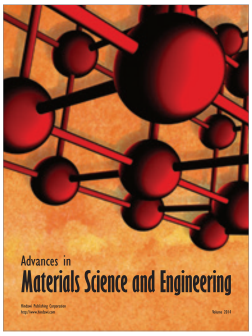
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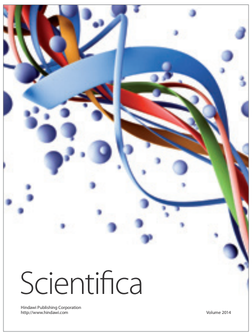
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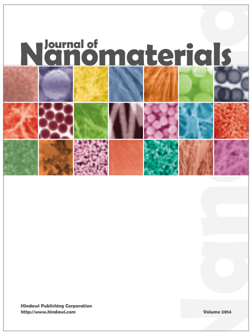
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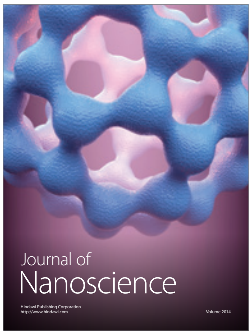
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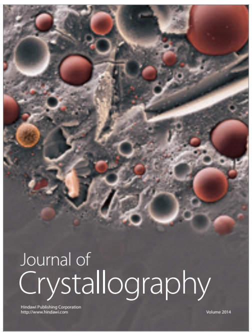
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