

# PZT Preparation by chemical root at low sintering temperature and studying its electrical properties



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## Abstract

Crystalline nanostructured (PZT) with atomic ratio of the Pb:Zr:Ti of 1:0.53:0.47 was synthesized by a chemical method starting from lead, titanium and zirconium salts; and using low temperature synthesis path which supposed to compose a nanostructured PZT. Using XRF, a qualitative analysis had carried out to investigate that the samples contain lead, titanium and zirconium. The samples were pressed as pellets 10mm diameter and 1mm thickness. Then sintered at 1100°C. Using high voltage generator a poling process were achieved at (0.5-1.5)KV/mm at room temperature. Using AC measurements, dielectric constant including real and imaginary parts were studied in a function of frequency in the range (20Hz-3kHz) for poled and unpoled samples at room temperature. The dielectric constant including real and imaginary parts were studied too in a function of temperature at constant frequency. Pyroelectric current was measured in order to calculate the pyroelectric coefficient of the material.

**Keywords:** PZT, ferroelectric, dielectric, poling process, pyroelectric.

## Resumen

Se sintetizó una nanoestructura cristalina (PZT) con razón atómica Pb: Zr: Ti de 1: 0,53: 0,47, por medio de un método químico a partir de plomo, titanio y sales de circonio; y se usó una ruta de síntesis de baja temperatura que se supone permite componer una nanoestructura PZT. Se hizo un análisis cualitativo con XRF, para conocer el contenido de plomo, titanio y circonio en las muestras. Las muestras fueron prensadas como pellets de 10 mm de diámetro y 1 mm de espesor. Posteriormente se sinterizaron a 1100°C. El proceso de polarización se logra con el uso de un generador de alta tensión al (0,5-1,5)KV/mm a temperatura ambiente. Se hicieron mediciones de corriente alterna, y de las constantes dieléctricas de las partes reales e imaginarias que se estudiaron en función de la frecuencia; en el rango de (20Hz-3kHz) para muestras polarizadas y no polarizadas, a temperatura ambiente. También se midió la constante dieléctrica de las partes reales e imaginarias que fueron estudiadas en función de la temperatura, a una frecuencia constante. Se midió la corriente piroeléctrica para calcular el coeficiente piroeléctrico del material.

**Palabras clave:** PZT, ferroeléctrico dieléctrica proceso, polarización, piroeléctrico.

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## I. INTRODUCCIÓN

Lead Zirconate Titanate,  $Pb(Zr_xTi_{1-x})O_3$  (PZT) ceramics are an important class of piezoelectric, pyroelectric and ferroelectric materials [1]. Due to their excellent dielectric, piezoelectric and electro-optic properties, they find a variety of applications in high energy capacitors, non-volatile memories (FRAM), ultrasonic sensors, infrared detectors and electro optic devices [2, 3, 4]. PZT alloys belong to the family of ceramics, which are alloys of lead oxide, zirconium oxide, and titanium oxide ( $PbO$ ,  $ZrO_2$ , and  $TiO_2$ ). The familiar structure of Perovskite appears in PZT alloys because there are equal numbers of divalent ( $Pb^{2+}$ ) and tetravalent ( $Zr^{4+}$  and  $Ti^{4+}$ ) cations. PZT alloys are in fact the alloys of two components:  $PbZrO_3$  and  $PbTiO_3$ . Thus, by controlling the composition and microstructure of the PZT alloys, it is possible to adapt their properties to suit particular applications [5]. The general chemical formula of our samples is  $PbZr_{1-x}Ti_xO_3$ , with  $x=0.47$ , due to the

peculiarities of PZT is that, in the transition zone in between the two structures ( $x= 0.53$ ), called morphotropic phase boundary (MPB), which has high dielectric constants and piezoelectric coefficients [6]. Polycrystalline ferroelectric materials (ceramics) may be brought into a polar state by applying a strong electric field (10-100 kV/cm), usually at elevated temperatures. This process, called poling, can reorient domains within individual grains along those directions that are permissible by the crystal symmetry and that lie as close as possible to the direction of the field. A poled polycrystalline ferroelectric exhibits piezoelectric and pyroelectric properties, even if many domain walls are still present. After the removal of the poling field, a ferroelectric material possesses macroscopic polarization, called spontaneous polarization PS [7, 8]. In this paper, chemical root is used to synthesize PZT at low sintering temperature. XRF is used to detect the composition. High voltage source was used to pole the samples, AC electrical measurements were used to study

the electrical properties and DC measurements were carried out to study the pyroelectric properties.

## II. EXPERIMENTAL

The low-temperature synthesis path followed by autocombustion process was adapted in this paper [2]. Lead nitrate ( $Pb(NO_3)_2$ ), titanium tetrachloride ( $TiCl_4$ ), zirconium oxychloride octahydrate ( $ZrOCl_2 \cdot 8H_2O$ ), analytical grade, were used as starting materials, titanium tetrachloride ( $TiCl_4$ ) and zirconium oxychloride octahydrate ( $ZrOCl_2 \cdot 8H_2O$ ) were solved in a distilled water at low temperature (about  $2^\circ C$ ) then a stoichiometric amount of ammonia was added to form a precipitate of  $TiO(OH)_2$  and  $ZrO(OH)_2$ . Adding nitric acid to the two solutions yielded  $TiO(NO_3)_2$  and  $ZrO(NO_3)_2$  solutions, then they added to the  $Pb(NO_3)_2$  solution with an appropriate amount of ethyl glycol which play two roles, one as a chelating agent and the other to provide the fuel for the autocombustion process. The atomic ratio of the Pb:Zr:Ti of solution was 1:0.53:0.47 with 2% excess of lead was introduced to compensate the evaporated amount during sintering process. After PZT precursor sol was obtained, the mixture was heated under  $100^\circ C$  until the gel formation.

Then the gel was calcinated at  $500^\circ C$  after that, the formed powder was pressed under 5 ton/cm as disks of 10mm diameter and 1mm thickness. The sintering was at  $1100^\circ C$  for 4 hours with temperature changes rate of  $5^\circ C/min$ .

Then they were tested by x-ray to investigate the structural characterization. The disks were polished and washed by alcohol. In addition, an air-dry silver paste was applied to the samples surfaces as electrodes, to ensure good electrical contact and introduce them for further characterization.

A small chamber was made to contain the sample. The chamber was made of ceramic and provided with terminals.

### A. Qualitative analysis

Using XRF device ,unisantis® type Si-PIN (liquid  $N_2$  free), energy resolution @ 5.9keV, Fe55 186eV, detection area  $7mm^2$ , and molybdenum (Mo) target operated at 50kV and 1mA, XRF spectrum was taken for the samples. Figure 1 reveals the existence of the three elements (lead, zirconium and titanium). Oxygen element was unable to be detected because it is out of the resolution of the device.

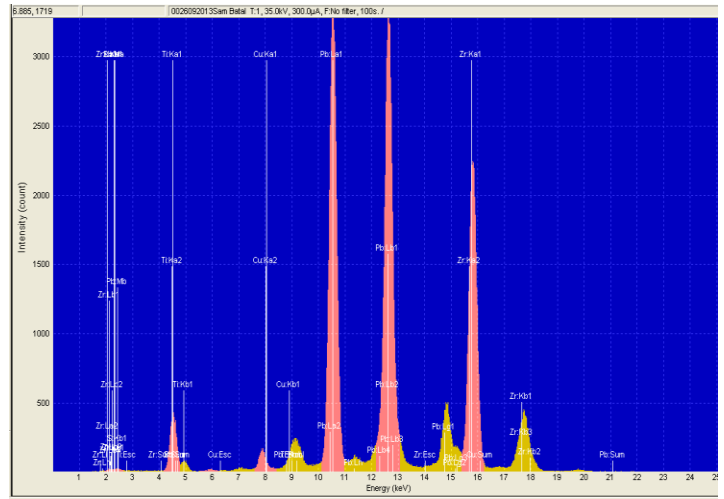
### B. Electrical characterizations

#### B.1 Electrical characterization for unpoled samples

The real and the imaginary parts of the dielectric permittivity were measured using RCL meter from MICROTTEST 6379 in the range of frequency (20Hz-3 kHz) at room temperature.

As shown in Figure 3, the real part of dielectric permittivity decreases sharply with increased frequency at

range (20Hz-100Hz), then it decreases slightly at higher frequency.



XRF spectrum for PZT sample.

**FIGURE 1.** Shows the XRD profile of the sample sintered at various temperatures which reveals the formation of the major tetragonal perovskite phase. From N. S. Gajbhiye *et al.* [2].

At frequencies below 1kHz, the four polarization mechanisms (electronic, ionic, orientational and space charge polarization) act. These polarizations involving the movements of charges either by orientation (*i.e.*, orientational polarization) or through the migration of charge carriers (*i.e.*, hopping or space charge polarization) belong to the relaxation regime. Because during the polarization or depolarization processes, a relaxation phenomenon occurs due to the time required for the charge carriers to overcome the inertia arising from the surrounding medium, in order to proceed in their movement. As the frequency increases above 1kHz, the only active polarization mechanisms.

Polarizations associated with vibrations of electrons (*i.e.*, electronic or optical polarization) or with vibrations of atoms or ions (*i.e.*, atomic or ionic polarization), this behavior belongs to the resonance regime, because at certain field is oscillation system.

The real part of dielectric constant close to the natural frequency of the vibration or frequencies a resonance will occur when the frequency of the excitation is given by Debye equation [9]:

$$\epsilon'_r = \epsilon'_{r\infty} + \frac{\epsilon'_{rs} + \epsilon'_{r\infty}}{1 + \omega^2 \tau_0^2} \quad (1)$$

Where  $\epsilon'_{rs}$  and  $\epsilon'_{r\infty}$  are the low and high frequency values of  $\epsilon'_r$ .

Figure 3 shows  $\epsilon_r''$  in a function of frequency. It's similar to the dielectric constant variation with frequency.

The values of  $\epsilon_r''$  decrease hundreds times before 1 kHz.

That can explained by Koop's model which state that at low frequency, grain boundaries are responsible for the high resistivity, and charges need relatively high energy to

hop between grains whereas at high frequency, grains are the responsible areas for conductivity and its resistivity is low [10]. So taking the hoping conductivity into account, the Debye equation can derived to become [9]:

$$\tan\delta = \frac{\omega\varepsilon_0(\varepsilon'_{rs}-\varepsilon'_{r\infty})\omega\tau_0+(1+\omega^2\tau_0^2)\sigma}{\omega\varepsilon_0(\varepsilon'_{rs}+\varepsilon'_{r\infty}\omega^2\tau_0^2)} \quad (2)$$

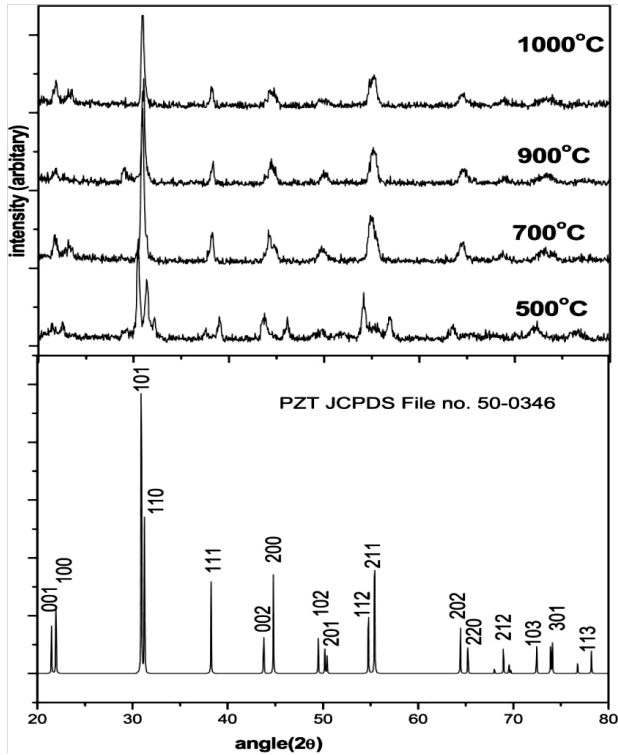


FIGURE 2. The XRD profile of the sample sintered at various temperatures.

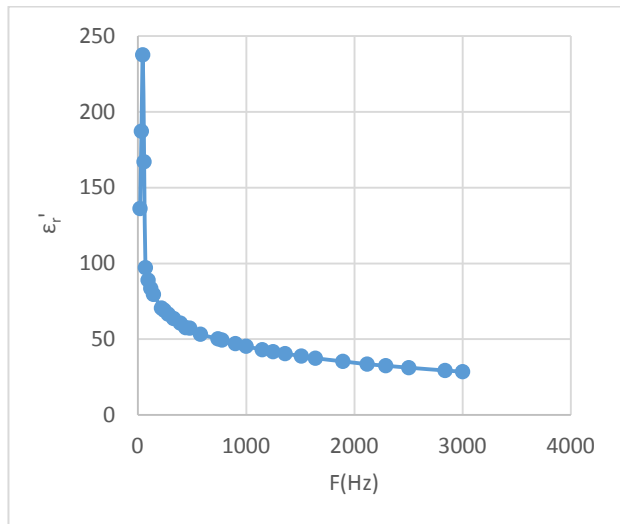


FIGURE 3. The real part of dielectric constant in a function of frequency at room temperature.

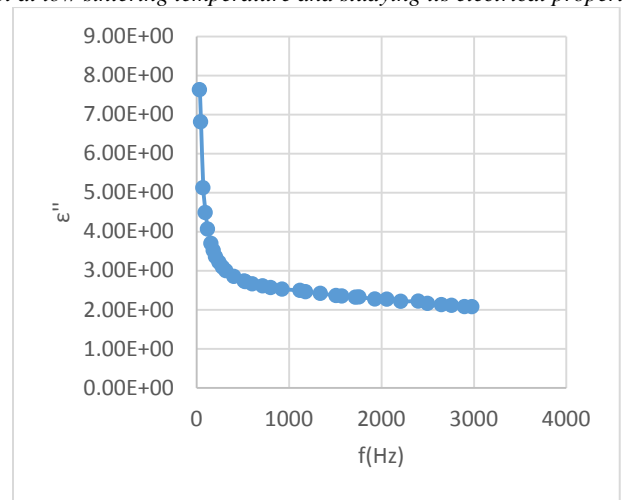


FIGURE 4. The imaginary part of the dielectric constant in a function of frequency at room temperature.

### C. Electrical Characterization for poled samples

For optimal poling, an electric field slightly higher than  $E_C$  (coercive field). Field should be applied at least for the switching time of the domains at room temperature [8]. A poled polycrystalline ferroelectric exhibits piezoelectric and pyroelectric properties, even if many domain walls are still present. After the removal of the poling field, a ferroelectric material possesses macroscopic polarization, called spontaneous polarization  $P_S$ .

Samples were submitted to an electrical field (1500V/mm, 1000V/mm and 500V/mm) for half an hour, dielectric measurements were achieved. Figures 5 and 6 represent the dielectric constant and dielectric loss factor as a function of frequency after poling with different poling electric fields. Poled samples show significant enhancement of the relative permittivity as the poling electric field is increased. Contrarily, the dielectric loss slightly decreased with increasing poling field especially at low frequencies.

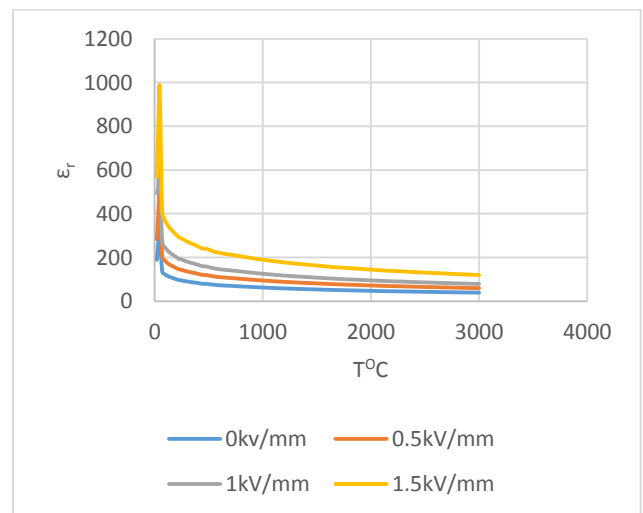
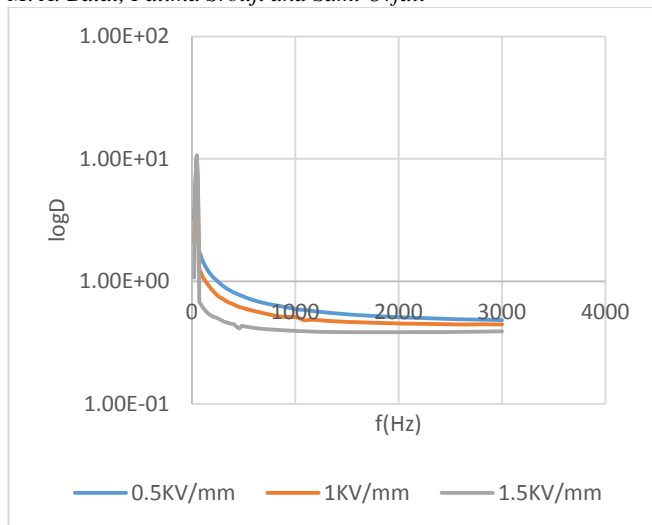


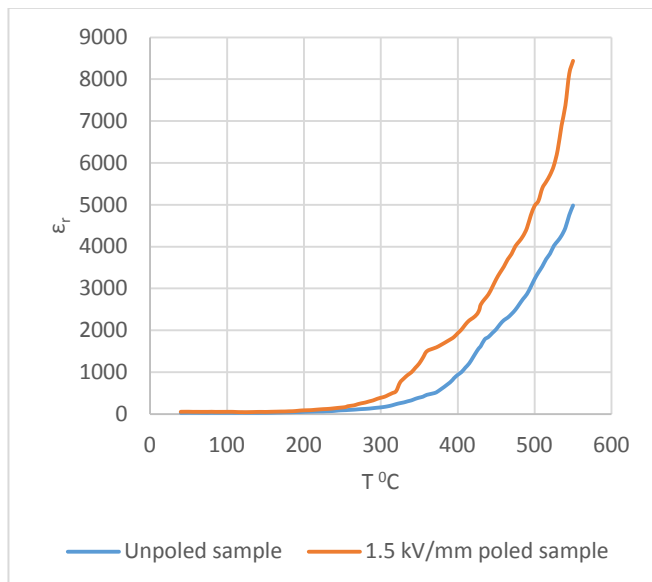
FIGURE 5. Dielectric constant variation with frequency at different poling field.



**FIGURE 6.** Logarithm of tangent  $\delta$  factor as a function of frequency after poling with different poling electric fields.

#### D. Pyroelectric characteristics

By changing the samples, the temperatures gradually up to 550°C, at about 5°C/min rate. The temperature dependence of the dielectric parameters at 1kHz for the 1.5kV/mm poled sample and the non-poled sample was measured. Figure 7 shows the dielectric constant changing with temperature. It exhibits relatively constant value up to 300°C at which the dipoles begin to align each other. The poling field (1.5kV/mm) shows significant enhancement of the dielectric constant, where many domains are already formed by mean of the poling field.



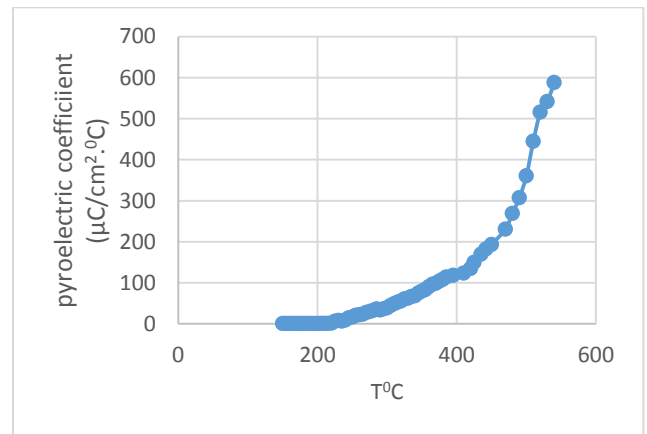
**FIGURE 7.** The dielectric constant variation in function of temperature for unpoled sample and 1.5kV/mm poled sample.

The pyroelectric current was measured using KEITHLEY 6517B electrometer then the pyroelectric coefficient  $p$  was calculated using the following relation [9, 10, 11]:

$$P = \frac{I_{Pyro}}{A} \left( \frac{dT}{dt} \right)^{-1} \quad (3)$$

Where  $A$  is the sample area,  $I_{Pyro}$  pyroelectric current. Figure 8 shows the pyroelectric coefficient  $P$  changing with temperature, it shows nonlinear variation with temperature.

As it shown, the pyroelectric coefficient exhibits low increasing with  $T$  in range of (200-400°C) and high increasing after  $T=400^\circ\text{C}$ .



**FIGURE 8.** Pyroelectric coefficient variation in function of temperature.

#### CONCLUSION

Dielectric constant values decreases sharply with increased frequency at range of (20-100kHz), then the dielectric constant decreases slightly in the range of (1-3).

Poling process increases the dielectric constant of the samples until certain poling voltage.

Poling process decreases the dielectric loops of the material especially at frequencies below 1kHz.

Poling field (1.5kV/mm) shows significant enhancement of the dielectric constant.

The pyroelectric coefficient exhibits high increasing with temperature after 400°C.

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