Studying The Electrical Properties Of Piezoelectric Material (PZT) Prepared By Organic Acid Precursor Method

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Abstract

The compound of piezoelectric nanopowders with a general system $PbZr_xTi_{1-x}O_3$ (PZT) at different concentrations (x =0.3, 0.5 and 0.7) were prepared by using organic acid precursor method. Disc shaped samples of each concentrations were sintered for two hours at temperatures in the range of (700-1100°C). The perovskite structure was determined by X-ray diffraction spectroscopy, and the dielectric properties were investigated for all samples. The dielectric studies of the compounds as function of temperature in the range (room temperature to 450°C) at frequency 1 KHz shows that the compounds undergo a phase transition of diffuse type from tetragonal phase to cubic phase. Maximum values of electrical properties such as (Dielectric constant 1200, loss factor 1.05) were found for $PZ_{0.5}T_{0.5}$ compounds, and these properties decrease with increasing of (Zr or Ti) additives. The effect of frequency in range (10^2-10^5 Hz) on electrical properties is low with stability in dielectric constant and dielectric loss.

Keywords: PZT ceramics, Dielectric properties, Piezoelectric.

دراسة الخصائص الكهربائية لماده إجهادية كهربائية PZT محضرة بطريقة خليط الحامض العضوي

الخلاصة

حضرت مركبات كهربائية اجهادية نانوية ذي الصيغة العامــة $PbZr_xTi_{1-x}O_3$ (PZT) عند (0.7 ,0.5 ,x=0.3) بطريقة خليط الحامض العضوي. صَنعت نماذج بشـــكل أقـــراص لمختلف التراكيز حيث اجريت عليها عملية التلبيد عند درجات حــــرارة (700- 1100 °C). وبأستخدام طيف حيود الاشعة السينية تم تحديد تركيب البيروفسكايت للنماذج المحضرة ومن ثــم فحص ودراسة خصائص العزل الكهربائي للعينات كدالة لدرجة الحرارة في المدى (درجة حرارة الغرفة الىC° 450) عند تردد 1KHz,والتي أظهرت بان المركبات تعاني أنتقالا"طوريــا مــن الرباعي الى المكعبي.كما تم الحصول على أعلى قيمة للخصائص الكهربائية مثل (ثابت العزل 1200 و عامل الفقد 1.05) عند النظام ($PZ_{0.5}T_{0.5}$) , في حين تقل هذه الخصائص مع زيادة الاضافة (Ti أو Zr) . تأثير التردد على الخصائص الكهربائية كان واطئا" ضمن المديات (Hz 10^5-10^3) مع استقرارية في ثابت العزل وعامل الفقد.

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1. Introduction

Piezoelectric materials can generate an electric charge with an applied load of pressure; conversely, they can change their physical dimensions with an application of an electric charge.

Conventional ceramic method (involve solid state reaction) and wet-chemical methods are generally utilized in the preparation of piezoelectric ceramic powders. Many materials, both natural and man–made exhibit the piezo-electric effect.These materials include naturally occurring crystals (Quartz, Rochelle salt) and Man – made ceramic; the family ceramics with peroveskite structures piezoelectric ceramic are in use today. In addition, there are some polymer compounds as piezoelectric [1, 2, and 3].

Lead Zirconate Tetanate (PZT) ceramics is widely used in piezoelectric applications, because of its superior piezoelectric properties. It covers a broad range of applications based on dielectric piezoelectric, pyroelectric, electro-optic and ferroelectric specialty properties, these applications include; firstly, piezoelectric ceramic is used in dielectric industry due to its high resistivity. Secondly: It is used in industry of ceramic electronic elements which are used in electric circuits due to high storage for power inside small volume, [4, 5].

Lead Zirconate Titanate is a binary solid solution of $(PbZrO_3)$ an anti-ferroelectric (orthorhombic structure) and a ferroelectric (tetragonal perovskite structure). PZT has a perovskit structure with Ti^{+4} and Zr^{+4} ions, which occupies the B site randomly. The two endmembers are (PT) that undergoes at $(490^{\circ}C)$ a simple phase transition from a paraelectric cubic to a ferroelectric tetragonal phase and (PZ) that behaves in a more complex fashion having a transition from cubic to an antiferroelectric orthorhombic phase [6,7] .

In the present investigation the studies cocerned on the electrical properties of a nano particle piezo-electric $(PbZr_xTi_{1-x}O_3)$ compounds with different concentration at x=0.3, 0.5 and 0.7 prepared by organic acid precursor method.

2. Experimental Techniques

Organic acid precursor method is used to preparation of PZT [8], and increasingly utilized to synthesis various ceramic powders. Preparation method of PZT powders can be described as follows; In order to obtain PZT powders, the first step is preparing aqueous solution of $(PbCl_2)$. In the second step, PZT powders are synthesized by adding $(ZrO_2$ and $TiO_2)$ powders to the aqueous solution of $(PbCl_2)$. Aqueous solution of oxalic acid is added to the result of step 2. The mole ratio of three compounds was 1:1:1.

The result of the above three steps is called "precursor". Then the mixture is stirred and heated up to $80^{\circ}C$ till a clear viscous resin is obtained. The precipitates are separated from the mother liquor by a filter-paper for twice with de-ionized water; the washed precipitates were oven-dried at 100 °C for two hours. The powders were pressed at about 2500 kg / cm^2 for 10 min. into disks 10.1 mm in diameter and 2-4mm in thickness. The samples are calcanited in the atmosphere air for two hours at 700 °C.The samples are grind and pressed, then sintered at 900 °C and

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1100 °C for two hours. All samples were polished after sintering. Electrodes on samples surface were coated by silver paste burning method. The poling process has been realized in transformer oil, bath under a DC electrical field of 1.5 kV/mm applied for 10min. at room temperature.

3. Result and Discussion
3.1. XRD Results and Analysis

3.1.1. XRD Pattern

Figure (1) shows the XRD pattern of $PZ_{0.5}T_{0.5}$ prepared in this work by chemical method at temperature 700 °C for two hours. The observed XRD peaks correspond to standard PZT patterns with low intensites. Some of peaks refer to PbO, $PbCO_3$ and TiO_2 phases. To clear strange phase, high temperature sintering above 700 ^{o}C was used.

Figure (2 (a-c)), show the XRD patterns of PZ_xT_{1-x} sample with various compositions of x = 0.3, 0.5 and 0.7 respectively, which are prepared at sintered temperature 1100 °C for 2 hours.

From Table (1) data of prepared compounds show a polycrystalline tetragonal PZT structure. The analysis illustrates the reflection from planes (001), (100), (110), (111) and (200) for each concentration. The peak value at (d-spacing = 2.85 °A and 2Ө = 31.36°) of the material PZT represents the major peak (110) which highest degree of crystallinity. Table (1), also shows that the values of (d-space) shifted to large values with the decreasing of Zr content x.

3.1.2 Structural Parameters

Structural parameters of unit cell in crystal structure (c, a), are calculated using tetragonal equation for all peaks for (PZ_xT_{1-x}) at (x = 0.3, 0.5 and 0.7).

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2\left(\dfrac{a^2}{c^2}\right)}} \ \ldots\ldots (1)$$

Table (2) shows values of volume (V) and c/a ratio. The ratio c/a > 1 suggests that PZT has perovskite structure with tetragonal phase.

3.1.3 Grain Size Measurement

The Scherer formula as mentioned below in equation (2) is used to estimate the crystillite size for the prepared samples.

Ultra fine powder (in nano size) was obtained from present preparation process of PZT, it is clear from Table (3) that increasing Zr content (x) leads to decrease the grain size of PZT and shows large grain size of PZT at ratio ($PZ_{0.3}T_{0.7}$).

$$t = \frac{0.9\lambda}{B\cos\theta_B} \ \ldots\ldots\ldots.. (2)$$

3.2 Microstructure

In order to study the microstructure of PZT (grain size and distribution), optical microscope is used. The optical photo-graphs for PZT grains which were sintered at 1100°C for 2hours, are illustrated in Figure (3 (a-c)), for ($PZ_{0.3}$ $T_{0.7}$), ($PZ_{0.5}$ $T_{0.5}$) and ($PZ_{0.7}$ $T_{0.3}$) respectively. These figures show different shapes of grains, some of them are irregular polygons shape, circular shape nearly, spherical and hexagons shape grains. Also the figures below illustrate the broad band distribution of ultra fine grains size.

The crystillite sizes that are determined in this image have an ultra fine microstructure with sub micrometer grains and that indicates

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to the absence of abnormal grain growth.

3.3 Bulk Density

In order to study the sinterability of the $PbZr_xTi_{1-x}O_3$ system, the bulk density of the sample was measured as a function of sintering temperature with different (x) as illustrated in Figure (4)**.** This figure shows that, the bulk density increases rapidly with temperature and reaches a maximum value at 1100 °C**.**

This figure also shows that the change in concentration of (x) for (PZ_xT_{1-x}) system is having small effect on bulk density.

3.4. Dielectric Constant and Temperature

The temperature dependence of the dielectric constant (ε_r) of (PZ_xT_{1-x}) system for (x = 0.3, 0.5 and 0.7) at 1 kHz is shown in Figure (5). It can be seen that the dielectric constant initially increases gradually with increasing temperature and shows a peak value of around $(\varepsilon_r = 1000, 1200$ and 1050) at (x = 0.3, 0.5 and 0.7) respectively.

The dielectric constant is reached maximum values at transition temperature from ferroelectric (tetragonal phase) to paraelectric (cubic phase), which is called Curie temperature (T_c), for $(PZ_{0.3}T_{0.7})$, $(PZ_{0.5}T_{0.5})$ and $(PZ_{0.7}T_{0.3})$. Table (4) shows values of dielectric constant at Curie temperature for different (x).

With increasing concentration of Zr, the transition temperature shows a shift towards smaller values of temperature as shown in Table (4), which exhibits a characteristic of relaxer material with diffuse phase transition. The broadening in phase transition is attributed to the structural disorder and compositional fluctuation present in the arrangement of cation at A-site and B-site with

lattice vacancies, leading to microscopic heterogeneity in the composition and thus results in the distribution of different local Curie points. The ferroelectric transition broadening will be caused by random in domains orientation.

The lower dielectric constant in the present investigation is caused by the effect of the ultra fine nano grain size (30-39 nm).

When the grain size decreases to values comparable to the width of domain walls, pinning points would develop inside the grain and the domain wall motion would be inhibited. The reduced wall mobility will cause a decrease in the relative permittivity.

3.5: Dielectric Loss and Quality Factor with Temperature

Figure (6) shows the variation in dielectric loss of (PZ_xT_{1-x}) system for (x = 0.3, 0.5 and 0.7) with temperature at frequency of 1 kHz. The dielectric loss exhibits a peak near the transition temperature, the values of dielectric loss for all concentration below Curie temperature, are approximate, while the values increase near the transition temperature region.

The dielectric loss peaks for the three concentrations can be divided into three parts according to their Curie temperature. The first part represents the contribution of orientation mechanism only, where, the contribution of the other mechanisms decreases as a result of decreasing the density due to heating. The second part is at Curie temperature where the polarization of orientation mechanism is approximately complete, while the third part above Curie temperature where the alignment of orientation dipoles is over due to thermal

vibration that leads to perturb the alignment. The last part comes from the contribution of the residual polarization mechanisms which decreases with temperature. The former reasons also affect the quality factor (Q), Figure (7) shows that, the quality factor reaches (Q =10, 12.5 and 20) at (x =0.7, 0.5 and 0.3) for (PZ_xT_{1-x}) system.

3.6. Rsistivity with Temperature

Figure (8) illustrates resistivity as a function of temperature for (PZ_xT_{1-x}) at   (x = 0.3, 0.5 and 0.7). With transition turn to cubic symmetry by increasing temperature, the resistivity transition turn from low amount (below Curie temperature), to high amount (above Curie temperature). That is caused where the dipoles in paraelectric state were over.

3.7 Dielectric Constant with Frequency

Figure (9) illustrates that relative dielectric constant of all the samples as a function of frequency with range of $(10^3 - 10^5$ Hz) at room temperature. It can be seen that the dielectric constant decreases gradually with increasing frequency. The fall in dielectric constant arises from the fact that the types of polarization don't occur instantaneously with the application of the electric field as charges possess inertia. The delay in response towards the impressed alternating electric field leads to loss and hence decline in dielectric constant.

At frequency of $(10^3 - 10^5$ Hz) the external field has a large effect on charges and dipoles movement, the three types of polarization mechanisms (orientation, Ionic and electronic) obey the external electric field while orientation polarization at that range contributes to polarization.

3.8. Dielectric Loss and Quality Factor with Frequency

Figure (10) shows the variation of dielectric loss of all the samples with frequency at range of $(10^3 - 10^5$ Hz) at room temperature. It can be seen that dielectric loss decreases with increasing frequency and exhibits approximate stability in these ranges.

Figure (11) shows the variation of quality factor with frequency, quality factor increases gradually with increase in frequency. Over a wide range of frequencies it is nearly constant.

4. Conclusions

Based on experimental results presented in this search, it is possible to draw the following conclusions. That PZT phase begins forming at temperature 700°C while complete reaction which leads to growth and stability phase occurs at temperature above 700°C. That effect replacement of Zr by Ti leads to fallowing (The values of $2\Theta^o$ were shifted to large values, these shifts occurred by d-spacing change and full in the grain size for PZT). Maximum values of electrical properties such as (Dielectric constant, loss factor) were found for $PZ_{0.5}$ $T_{0.5}$, and these properties decrease with increases Zr or Ti. Bulk density increases rapidly with increase in temperature. The electrical properties depended on nano PZT grains and the high density, the broad dielectric constant and dielectric loss peaks which indicate the domain orientation is random and this tends to broaden the ferroelectric transition, this is an important property in microwave devices applications. That effect of frequency

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in range (10^3-10^5 Hz), on electrical properties is low and stability in dielectric constant and dielectric loss, where this stability is an important property in tunable devices applications.

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Table (1) Comparison ($2\Theta^o$ and d A^o) between JCPDS and

PZ_xT_{1-x} for (x = 0.3, 0.5 and 0.7) prepared at $1100C^o$

STD.For,$PZ_{0.5}T_{0.5}$			X=0.3		X=0.5		X=0,7	
hkl	$2\Theta^o$	d A^o	$2\Theta^o$	d A^o	$2\Theta^o$	d A^o	$2\Theta^o$	d A^o
001	21.41	4.14	21.46	4.135	21.48	4.13	21.54	4.12
100	22	4.03	22.66	3.92	22.75	3.9	22.78	3.899
110	31.36	2.85	31.43	2.84	31.48	2.839	31.52	2.835
111	38.25	2.35	39.07	3.3	39.2	2.295	39.29	2.29
200	44.87	2.01	43.73	2.01	44.03	2.052	44.08	2.054

Table (2): Values of (c/a) and (V A^3)   for $PZ_x T_{1-x}$

(PZ_xT_{1-x})	c/a	V $(^oA^3)$
X=0.3	1.032	65.92
X=0.5	1.029	66.41
X=0.7	1.029	66.43

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Table (3): the grain size measurement for the prepared samples.

$PZ_x T_{1-x}$	c. s. (nm)
X=0.3	39
X=0.5	36
X=0.7	30

Table (4) Values of Dielectric constant at Curie temperature for $PZ_x T_{1-x}$

$PZ_x T_{1-x}$	Dielectric constant (ε_r)	Curie temperature (^{o}C)
X=0.3	1000	440
X=0.5	1200	370
X=0.7	1050	320
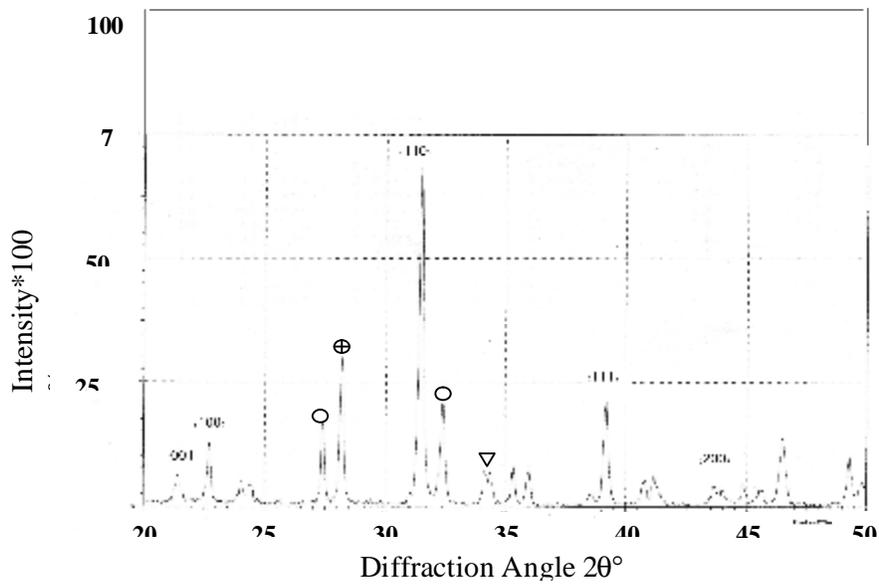
Figure (1) XRD patterns of $PZ_{o.5}T_{0.5}$ prepared at 700C^o for 2h.

O=PbCO$_3$, Ñ=PbO, Å = TiO$_2$

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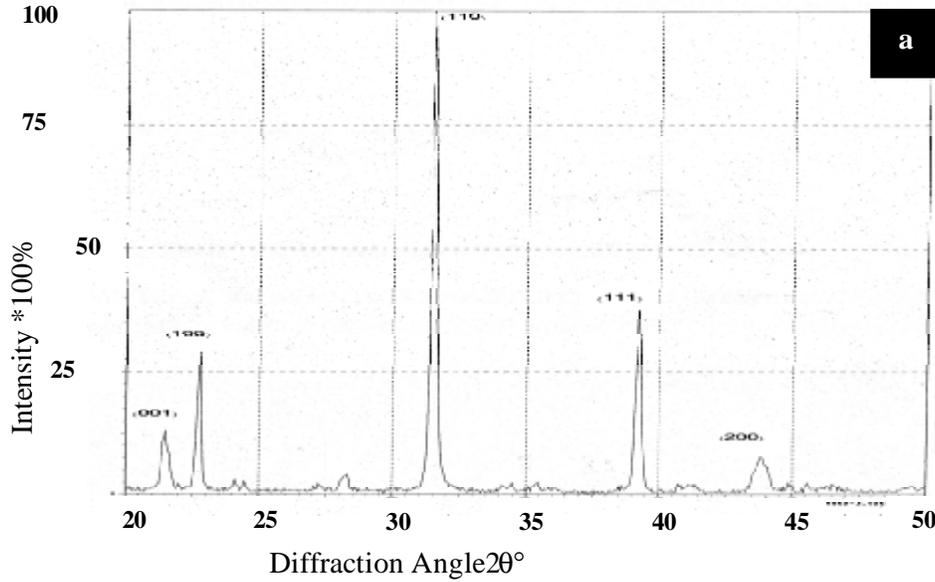
Figure (2-a) XRD patterns of PZ_xT_{1-x} prepared at 1100 C° for 2h. for (a) X=0.3
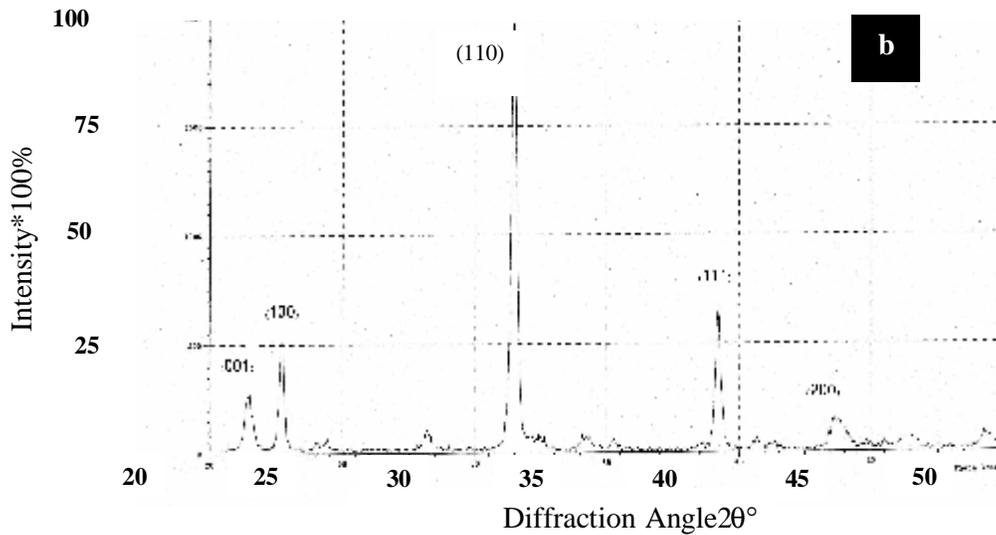
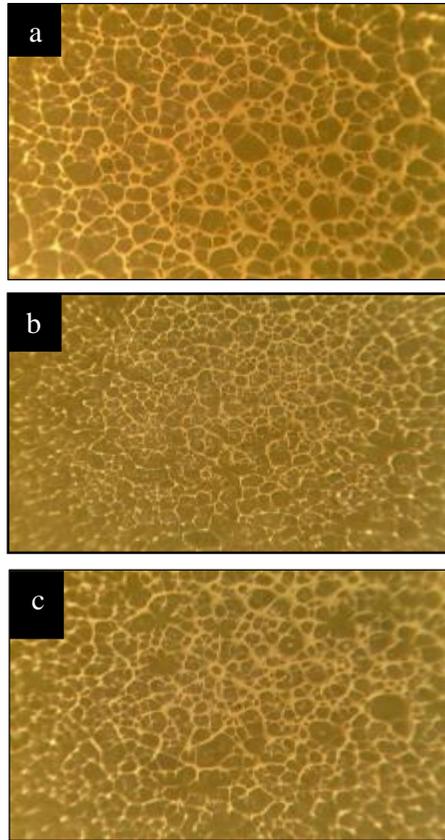**Figure (2-b) XRD patterns of PZ_xT_{1-x} prepared at 1100 C° for 2h. for (b) X=0.5**

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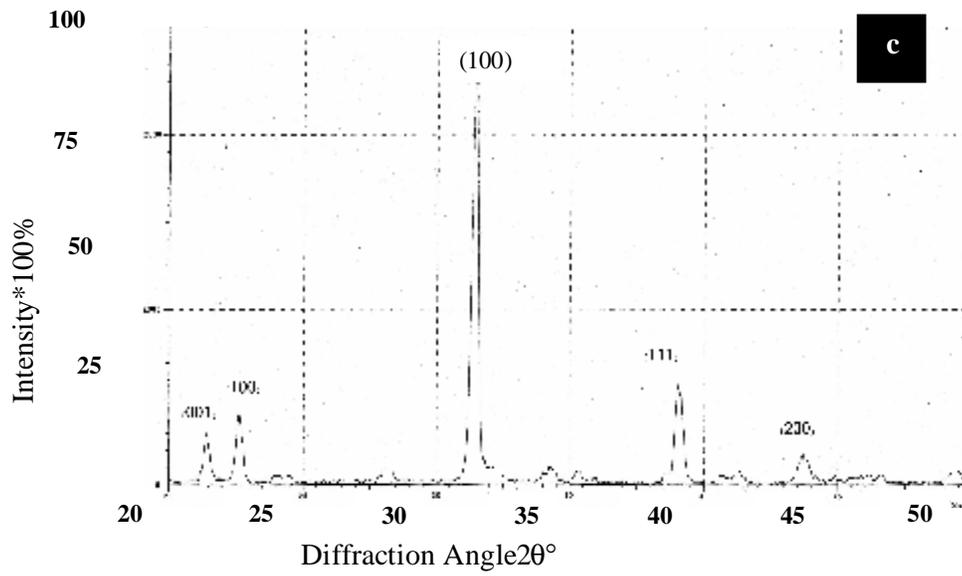
Figure (2-c) XRD patterns of PZ$_x$T$_{1-x}$ prepared at 1100 C$^°$ for 2h. for (c) X=0.7

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`figure (3): Optical microscope image for
PZ$_x$T$_{1-x}$, M= 600X for (a) X=0.3,
(b) X=0.5 an (c) X=0.7
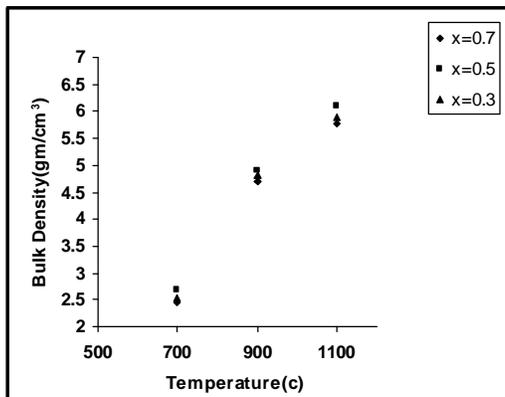
**Figure (4) Variation bulk density with
temperature for (PZ$_x$ T$_{1-x}$) at x=0.3, 0.5, 0.7**
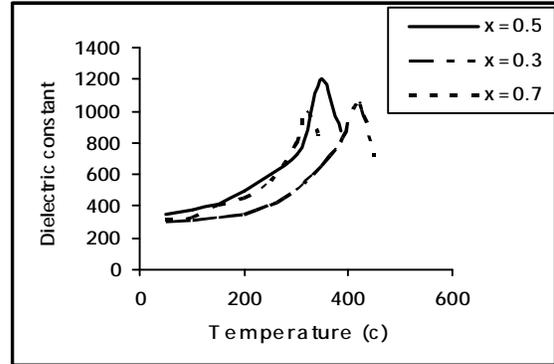
**Figure (5) Variation of Dielectric Constant ε$_r$
with Temperature c^0 at 1 KHz for (PZxT1-x)
at x= 0.3, 0.5 and 0.7**

**Figure (6) Variation of Dielectric Loss (tarδ)
with Temperature (^{0}c) at 1 KHz for (PZ$_x$ T$_{1-x}$)
at x=0.3, 0.5 and 0.7**

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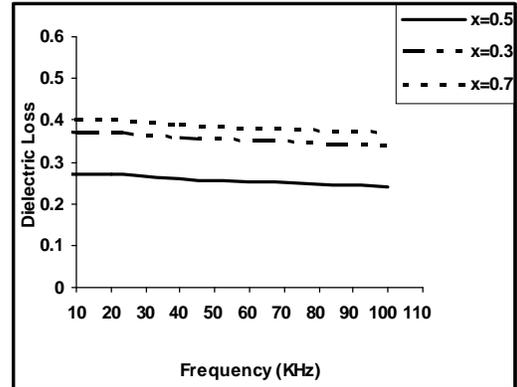**Figure (7) Variation of Quality Factor with Temperature at 1 KHz for (PZ$_x$T$_{1-x}$) at x=0.3, 0.5 and 0.7**

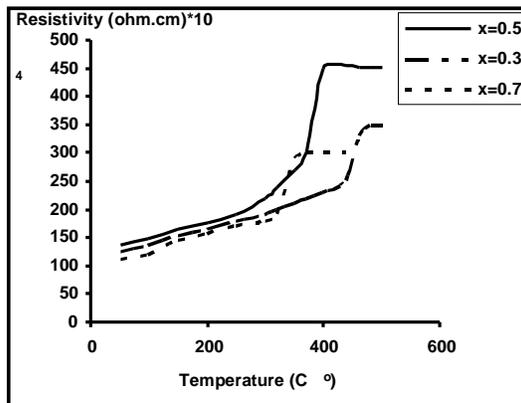**Figure (10) Variation of Dielectric Loss (tanδ) with Frequency (Hz) for (PZ$_x$T$_{1-x}$) at x=0.3, 0.5 and 0.7**

Figure (8) Variation of resistivity (Ω.cm) with temperature (°C) at 1 KHz for (PZ$_x$T$_{1-x}$) at x=0.3, 0.5 and 0.7
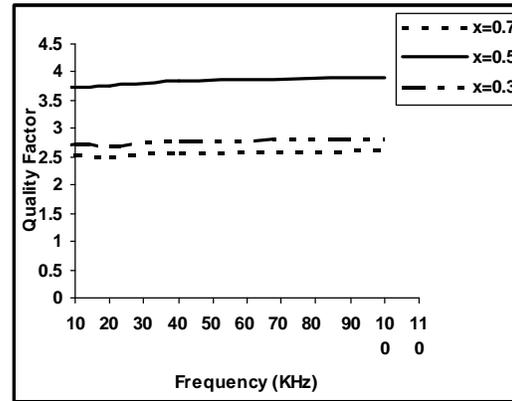

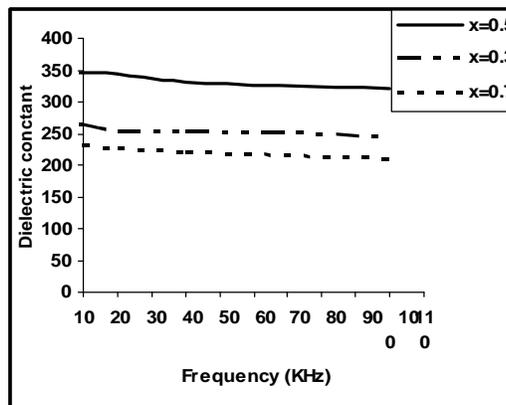**Figure (11) Variation of Quality Factor with Frequency (Hz) for (PZ$_x$T$_{1-x}$) at x=0.3, 0.5 and 0.7**

Figure (9) Variation of Dielectric Loss (tanδ) with Frequency (Hz) for (PZ$_x$T$_{1-x}$) at x=0.3, 0.5 and 0.7