The effect of temperature on the dielectric properties of Lead Titanate $PbTiO_3$

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Abstract:

The lead titanate $PbTiO_3$ was prepared by solid state reaction method . In this method ,the mixture of (PbO : TiO_2) compounds in mole ratio [1:1] was calcined at 900 ^oC for 2 hr. The crystallisation and growth of tetragonal $PbTiO_3$ phase (c/a =1.039) were investigated by using XRD technique. The dielectric properties of $PbTiO_3$ were reported, in which the dielectric constant of $PbTiO_3$ increases with increasing temperature in tetragonal phase to reach maximum value at curie temperature (486 ^oC) ,then decreases with increasing temperature in cubic phase. The loss factor increases with increasing temperature in different ratios The electric resistivity of $PbTiO_3$ decreases with increasing temperature.

تأثير درجة الحرارة على خواص العزل الكهربائي لمادة تيتانيت الرصاص $PbTiO_3$

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ملخص البحث:

تم تحضير مادة تيتانيت الرصاص $PbTiO_3$ باستخدام طريقة تفاعل الحالة الصلبة. في هذه الطريقة تم حرق خليط المركبين (PbO : TiO_2) وبنسبة مولية [1 : 1] بدرجة حرارة حرق ^oC 900 ولمدة 2 hr ؛ تم التحقق من تبلور ونمو الطور الرباعي لمادة $PbTiO_3$ (c/a=1.039) باستخدام تقنية حيود الأشعة السينية؛ تم قياس خواص العزل الكهربائي لمادة $PbTiO_3$, حيث إن ثابت العزل لهذه المادة في الطور الرباعي يزداد مع زيادة درجة الحرارة ليصل أعلى قيمة له عند درجة حرارة كوري (486^oC) ومن ثم ينخفض مع زيادة درجة الحرارة

في الطور ألمكعبي؛عامل الفقد لمادة $PbTiO_3$ يزداد مع زيادة درجة الحرارة وبمعدلات مختلفة بينما تنخفض المقاومية الكهربائية مع زيادة درجة الحرارة.

Introduction:

Lead titanate $PbTiO_3$ is a perovskite ferroelectric having a high curie temperature of 490 °C. $PbTiO_3$ ceramics having a very small aging rate of dielectric constant, and have a small dielectric constant as compared with those of piezoelectric ceramics such as $BaTiO_3$. Therefore $PbTiO_3$ ceramics would be of great promise as a stable piezoelectric material for high temperature and high frequency applications [1]. $PbTiO_3$ ceramics have many important ferroelectrical and piezoelectric technological applications in optoelectronics and , microelectronics, because of their polarization [2].Various techniques have been applied to prepare lead titanate powders such as sol-gel method [3,4,5], hydrothermal method at 110-200 °C [6] and solid- state reaction of mixed oxides [7,8,9], they reported that $PbTiO_3$ is highly sensitive to the addition of certain cations, in which Niobium accelerate the densification process, increases the concentration of the lattice vacancies.

The objective of this paper is to prepare lead titanate $PbTiO_3$ phase with good growth and to demonstrate that lead titanate can be produced by solid-state reaction with a good dielectric properties.

Experimental section:

1-Synthesis:

To prepare $PbTiO_3$ ceramic , PbO (purity 96 % - BDH) and TiO_2 (purity 98 % - BDH) were the chemicals chosen as starting raw materials and that were weighed according to the stoichiometric formula of the required composition in the phase diagram of PbO-TiO_2 system [10].By using solid- state reaction method, these chemicals were mixed with equal molar ratios with excess in PbO compound by (2.2 wt%) because the loss in the weight of PbO compound in the calcination process [11].The mixture was finely powdered using an agate mortar to obtain homogenous mixture and further grounded after adding ethanol. It was preheated at 400 °C for 30 min and cooled to room temperature .Then ,the mixture was further grounded and calcined at 900 °C for 2 hr .

The powder of calcined material was pressed into pellets in 20 mm diameter and 5 mm thickness. These pellets were sintered at 1000 °C for 1 hr.

2- Characterization:

2.1- X-ray diffraction:

The calcined material was evaluated by using XRD analysis type PHLIPS PW1316/90 single open recorder / CuK_α target .

The structural parameters (a) and (c) were calculated using following equation[12] :

$$d_{hkl} = \frac{a}{[h^2 + k^2 + l^2 (a^2/c^2)]^{1/2}} \quad \text{……(1).}$$

Where d_{hkl} = d in Braggs law ($n\lambda = 2d\sin\Theta$) , n=1 and λ= 1.54 .

2.2-Dielectrical properties:

The electrical resistance for a group of samples was tested using Ohm-meter with temperatures (32-250 ºC) after prepared by applying a silver electrode on surfaces of each samples . The electrical resistivity (ρ) was calculated using the equation (2). The capacity (C_p) and the resistance of $PbTiO_3$ material in C-R circuits (R_p) were measured using (Agilent 16451 Dielectric Test Fixture) with temperatures (30-490 ºC) at 10 KHz. The dielectric constant (ε_r) and the loss factor(ε_r'') were calculated using the equations (3) and (4), respectively .

($\rho = R\,A/d$) ………….. (2)

$\varepsilon_r = C_P\, d / \varepsilon_o A$ ………. (3) .

$\varepsilon_r'' = d / \omega\, \varepsilon_o R_p A$ ………. (4).

Where, A: surface area of sample , d : thickness

Results and discussion:

Figure (1) shows the XRD pattern of the prepared PbTiO3 phase. This figure shows a good growth in tetragonal $PbTiO_3$ phase (a=4.03,c=4.19) and (c / a= 1.039), addition to appearance all main peaks that recognize the tetragonal $PbTiO_3$ phase such peaks (001), (100), (101), (110), (111), (200), (102) at 2 theta (22.6), (23.1), (31.3), (32.3), (39.1), (46.4), (49.8), respectively with high purity. Also this figure shows that there is a shift in 2 theta by (+ 0.2 degree) by compare it with the XRD patterns of $PbTiO_3$ that observed by Wang et al [3] and Nakagawa et al [13].

Figures 2,3,4 shows the dielectric constant , loss factor and electrical resistivity of $PbTiO_3$ material as a function of temperature, respectively.

Figure (2) shows that the dielectric constant of $PbTiO_3$ material increases slowely rate with increasing temperature in range (32-260 °C), then stay stable until (300 °C). After that, the dielectric constant increases in high ratios with increasing temperature until reaching maximum value (1183) at curie temperature (483 °C). In general , the dielectric constant increases with increasing temperature in the tetragonal $PbTiO_3$ phase and then ,it decreases with increasing temperature in cubic $PbTiO_3$ phase. This difference in behavior of the dielectric constant is because the change in the crystal structure of $PbTiO_3$ from tetragonal to cubic phase, which leads to change in the dielectric properties of piezoelectric materials with temperature [1].

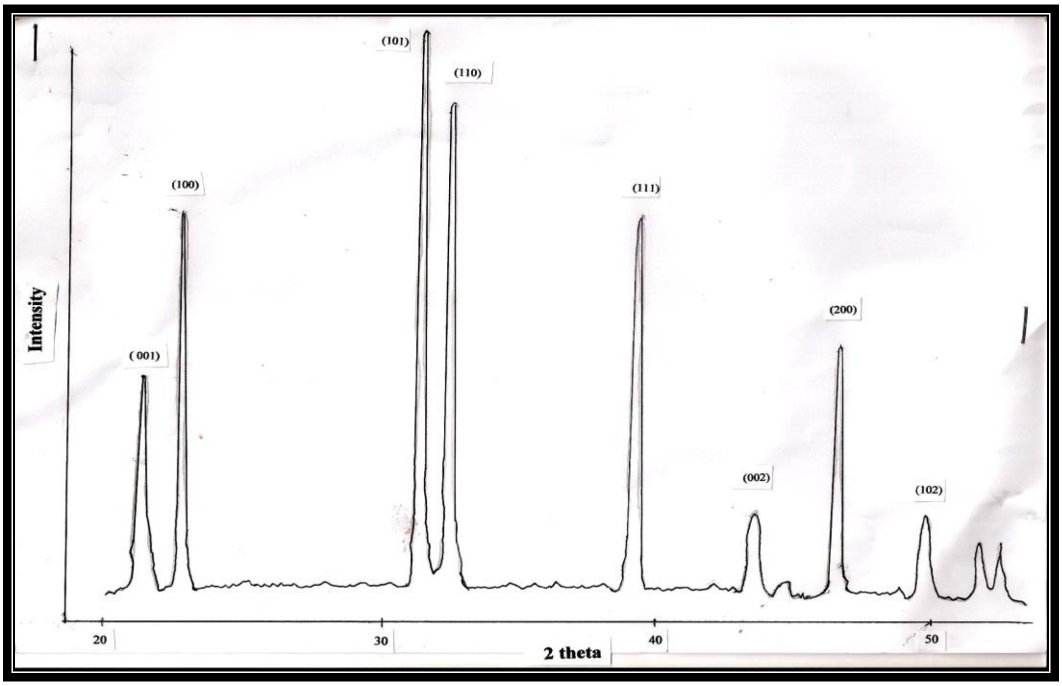

Fig.1: XRD pattern of prepared $PbTiO_3$ phase at 900 °C for 2 hr.

The measured curie temperature was less than the theoretical value (490 °C) by (- 4 °C), this shift because of the impurities in the starting materials. Figure (4) shows that the loss factor of $PbTiO_3$ material increases with increasing temperature. To explain this behavior, the loss factor represents the loss in energy in the electric, dielectric materials, but in dielectric materials the loss in energy is variable and depending on the type of material, in which energy that is required to brake the resistance of viscous medium (interior friction) decreases with increasing temperature and that means, increasing in the alignment speed of dipoles and appearance the loss in the energy immediately [14].

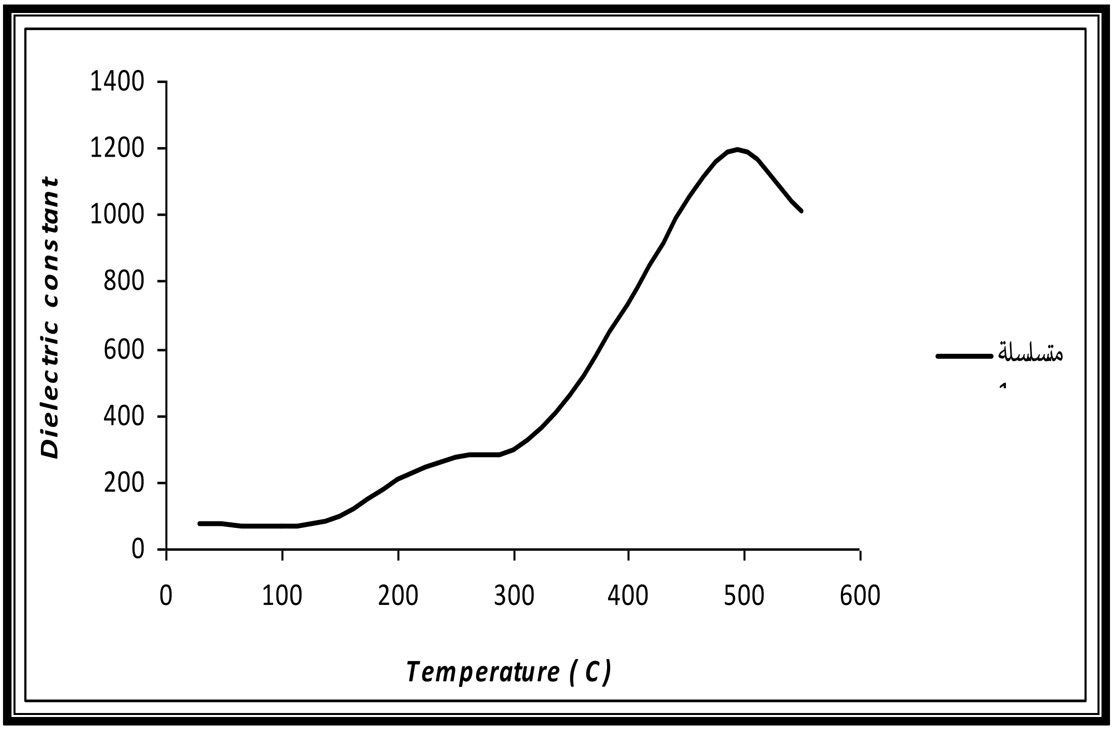

Fig.2: Dielectric constant of $PbTiO_3$ as a function of temperature

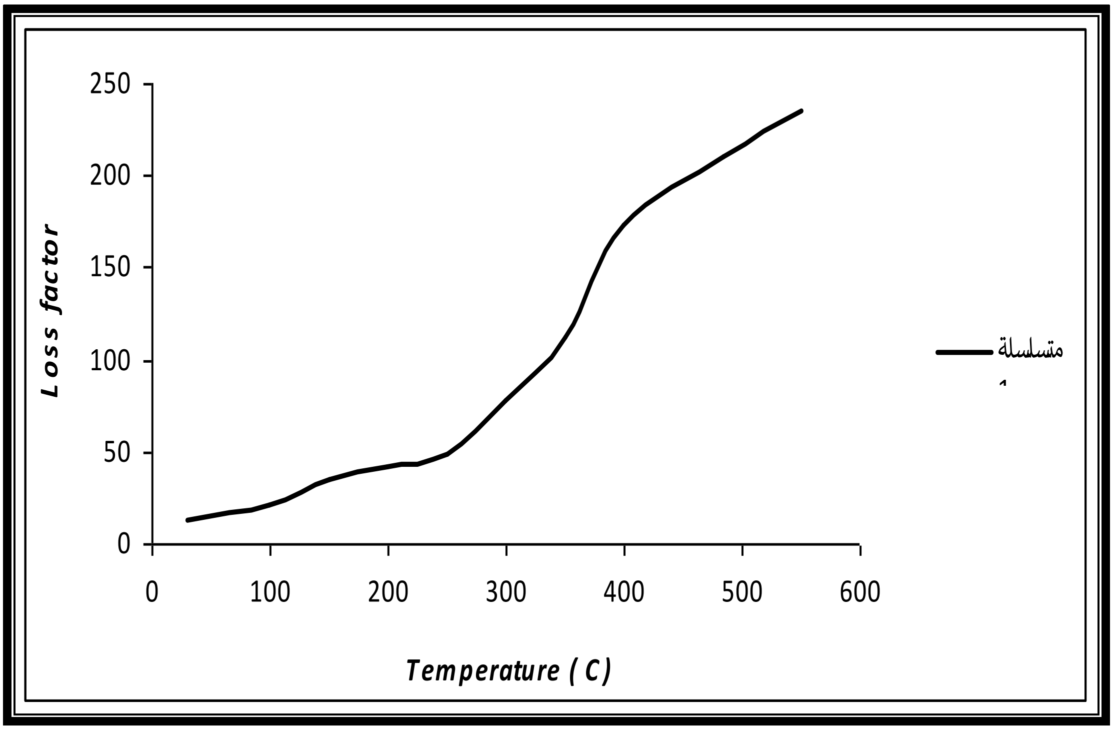

Fig.3 : Loss factor of $PbTiO_3$ as a function of temperature.

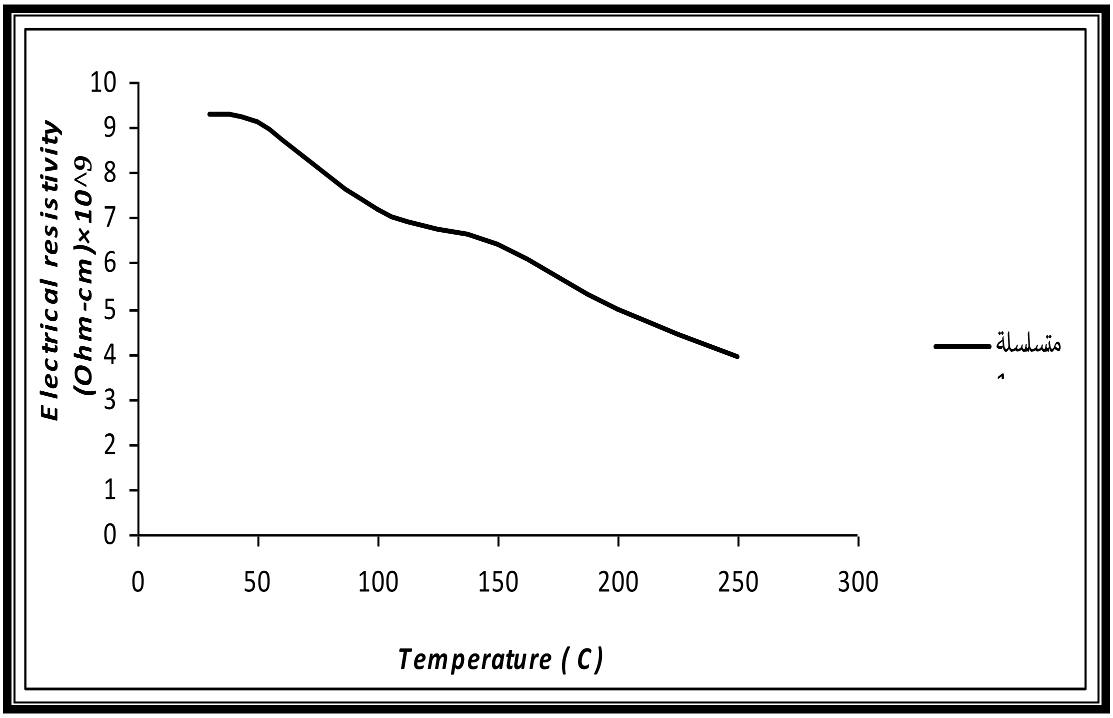

Fig.4: Electrical resistivity of $PbTiO_3$ as a function of temperature

Figure (4) shows that the electrical resistivity of $PbTiO_3$ material decrease with temperature increase ,in which a sharp decreasing over two temperature ranges (45- 103 C), up to 160 C and semi stable region in electrical resistivity over the temperature range (105-150 C).

From this figure, it can be seen that the electrical resistivity strongly depend on the temperature .This behavior can be explained as follows: the electrical conductivity of dielectrics may be either ionic or electronic or both. Ionic conductivity(σ) is simply due to the migration of positive or negative ions and it changes with temperature according to the equation

$$\sigma = \sigma_o \exp(- E_a / K_B T) \quad \ldots\ldots\ldots\ldots (5)$$

Where E_a is the activation energy, K_B is Boltsmanns constant and T the absolute temperature. From equation (5) , it can be seen that the electrical conductivity increases. In other words, the electrical resistivity decreases with increasing temperature . Electronic conductivity in dielectrics arises from modification to the quantum mechanical band theory of solids, in which , at any finite temperature, electrons will be thermally excited into conduction levels, that lead to decreasing the electrical resistance [15].

Conclusion:

The lead tianate $PbTiO_3$ material prepared with good growth , purity in solid-state reaction method by calcination the mixture of($PbO-TiO_2$) as a raw materials at 900 C for 2 hr. The dielectric properties of $PbTiO_3$ material strongly depend on the temperature ,in which the dielectric constant increases with increasing temperature in tetragonal phase and it decreases with increasing temperature in cubic phase , the loss factor of $PbTiO_3$ material increases with increasing temperature and the electrical resistivity decreases with increasing temperature obviously.

References:

1- Rosen C.Z, Basavaj V, Newnham R; Piezoelectricity ; American Ins.phys.-New York, P175, 1992.

2- Chilibon, Marat J , Igrija R ; Ultrasound role in Sol-Gel processing of $PbTiO_3$ ceramics; J. Optoelectronics and advanced mater,Vol.7, No.5 P 2727, 2005.

3- Wang Y, Xu G,Yang L ,Ren ; Preparation of single-crystal $PbTiO_3$,nanorods by phase transformation from Pb_2TiO_6 nanorods; J. Alloys and compound, Vol.481, P127,2009.

4- http//www. j: $ptio_3$ sol 5.htm

5- Baodong Q ,Yuguo W, Peilin Z ; Sise and temperature dependence of dielectric constant of ultra fine $PbTiO_3$ particles ; Chin.phys.lett, Vol.11, No.8, P514, 1994.

6- Chien A T, Sachlaben J,Kim J H,Speck J S; Synthesis and characterization of $PbTiO_3$ powders and heteroepitaxial thin films by hydrothermal synthesis; J.Mater.Res, Vol.14 ,No.8, 1999.

7- http// $PbTiO_3$-PbZ_rO_3 - $Pb(Mn_{1/3}$-$Nb_{2/3})O_3$// 1310-0157,2007.

8- Chandaratreya S S,Fulrat R M ; Reaction mechanisms in the formation of PZT solid solution ; J.Am.Cermic.Soc, Vol.64,No.7, P422, 1981.

9- http// resources .metapress .com/ pbf-preview.axd.-J.Mater.Sci.lett, Vol.11,1992.

10- Barnard J,William R C; Piezoelectric ceramic; Acadimic press,P117 1971.

11- Othmer K; Encyclopedia of chemical technology; Vol.10,P13, Wiley-Inter,Pub, 1980.

12- Cullity B D; Elements of x-ray diffraction; Addison-Wesley Pub. Co.Inc,1967.

13- Nakagawa T, Yanaguchi J, Okuyama M; Preparation of $PbTiO_3$ ferroelectric thin films by chemical vapor deposition; Jap.J.Appl Phys,Vol.21,P655,1982.

14- Harrop P J, ; Dielectrics; Buttelworth-London 1972.

15-Odwyer J J ; The theory of electrical conduction and breakdown in solid dielectrics ; Clarendon Press. Oxford 1973.