International Journal of Latest Research in Engineering and Technology (IJLRET)
ISSN: 2454-5031
www.ijlret.com‖ Volume 2 Issue 4‖ April 2016 ‖ PP 42-49

Structural, optical and electrical properties of PbTiO3 nanoparticles prepared by Sol-Gel method

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ABSTRACT: Lead titanate ($PbTiO_3$; PT) powders were successfully prepared by a sol –Gel technique. PT powders were heated at various calcination temperatures, ranging from 500 to 1000 ºC, for 2 h at a heating/cooling rate of 5 ºC/min. Both X-Ray diffraction and transmission electron microscopy investigations showed that well crystalline pure phase $PbTiO_3$ nanopowders have been synthesized after calcination of the $PbTiO_3$ gel at 1000 ºC. The second phases such as PbO, and TiO_2 were detected in the powders calcined below 1000 ºC. The optical properties have been studied by UV-VIS spectroscopy. Morphology and structures have been determined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Electrical properties were measured for deferent annealing time.
Keywords: Ceramics, ferroelectrics, nanoparicles, optical properties, electrical properties.

I- INTRODUCTION

Ferroelectric ceramics are important electronic materials that have a wide range of industrial and commercial applications, such as high-dielectric constant capacitors, transducers, sensors and ultrasonic motors [1]. Among perovskite ferroelectric materials, lead titanate ($PbTiO_3$ or PT) ceramics have been investigated extensively. Perovskite systems (ABO_3) have been studied widely for its B site substitutions [2-3]. Basically, interest in these systems is due to their potential applications as ferroelectric materials. The improvement in the piezoelectric and pyroelectric properties is also described by replacing Pb in the A site of the ABO_3 structure [4–6]. Prominent Lead titanate ($PbTiO_3$) has a perovskite crystal structure, with a relatively high Curie point of 4900C. Large c/a ratio in $PbTiO_3$ at low temperature confer tetragonal phase, it disintegrates into powder when cooled through the Curie point [7]. There are a lot of processing techniques for preparing PT powders, such as the solid state reaction technique [8], the sol-gel method [9] molten salt synthesis [10] and the hydrothermal technique [11]. Some authors have already reported various methods of preparation of $PbTiO_3$ nanopowders such as conventional mixed-oxide, Pechini-type processes, mechanochemical synthesis, hydrothermal process, sputtering, spray drying and sol-gel processing [12 13, 14, 15, 16, 17]. Among them, the sol-gel methods have the advantages of being cheap and simple and precise control of the composition. In this work PT powder was prepared by the sol –gel method and the effect of sintering temperature on the structural, and the optical and electrical are operating.

II- EXPERIMENTAL PROCEDURE

The $PbTiO_3$ powders nano-particles were prepared by Sol-Gel method . The raw materials used were commercially available lead carbonate ($PbCO_3$) and titanium dioxide (TiO_2) (Alfa Aesar a Johnson matthey Co.). 0.2 mol of NaOH was dissolved in 100 ml distillated water , 0.1 mol of lead carbonate was added to the NaOH solution . The mixture was magnetically stirred for 1 hour. Filtering have been performed then it added to 100 ml distillated water and 0.1 mol of titanium dioxide .The mixture was magnetically stirred for 2 hour. Then, the mixture powders were calcined using various calcinations temperatures,500 ,600,700,800,900 and 1000 ºC, for 2 h at a heating/cooling rate of 5 ºC /min. . X-ray diffraction (XRD) was employed to identify the phase formed. The particle morphology and size were directly imaged; using transmission electron microscopy (TEM) and the average particle size was determined by using Sherrure method. The powder are pressed into discs of 7.5mm diameter and 1~ 1.5cm thickness at 20 MPa. The pressed disks were placed in small silica crucible which was placed at the center of big crucible and covered with aluminum oxide. The sintering temperatures (Ts) for the disks was 1100 °C at sintering time (ts) equals to 2 hours. Finally, the disks were mechanically

treated for producing samples with 7.5mm diameter and about 1.5mm thickness and were coated with aluminum thin film.

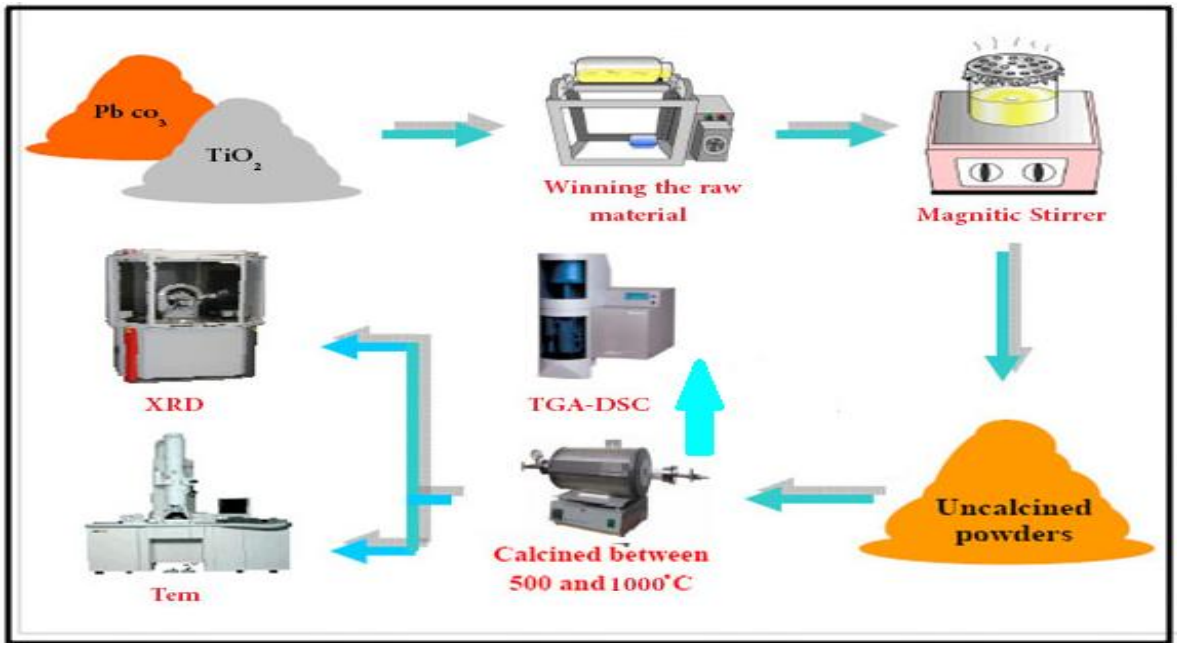


Fig.1: The block diagram of sol-gel preparation method.

III. RESULTS AND DISCUSSION

III.1. X-RAY DIFFRACTION:

The powder XRD patterns were obtained for the powders calcined at 500°C, 600°C, 700°C, 800°C, 900°C and 1000°C using XRD (EMMA) GBC diffractmeter in the range of Bragg's angle (2θ) 20°- 60° and these patterns are shown in Figure. 4.1. It is clear from the figure that, in the case of the sample calcined at 500 °C, crystallization start to form the perovskite PT phase along with small impurities of PbO and TiO_2. The XRD patterns for the samples calcined at temperatures 600°C and 700°C also show that the perovskite phase is observed along with the PbO phase. However, this impurity phase is found to gradually decrease from 700°C to that calcined at 800°C.

For the sample calcined at a temperature of 900°C, PbO still appears and the peaks of the perovskite phase are observed clearly confirming the formation of PT. Thus, it is observed that the PbO phase gradually decreases with the increase of calcination temperature from 500 °C and it disappears at 1000°C. A sharp intensity peak (2θ = 31.85°) indicates the formation of perovskite PT phase which can be matched with the JCPDS file no. (06-0452). The XRD pattern clearly shows no unwanted phase formation like TiO2 or PbO at 1000 °C, indicating that the sol-gel process used in the present study is a suitable technique for the preparation of PbTiO3 Nano particles. The broad XRD peaks clearly indicate the presence of nanocrystallites particles. From the XRD patterns, the crystallite size was calculated with the help of Scherer's formula ($t = 0.9\lambda/\beta\cos\theta$) (where λ – wavelength used, β – Full Width at Half Maximum (FWHM) and θ - diffraction angle) .

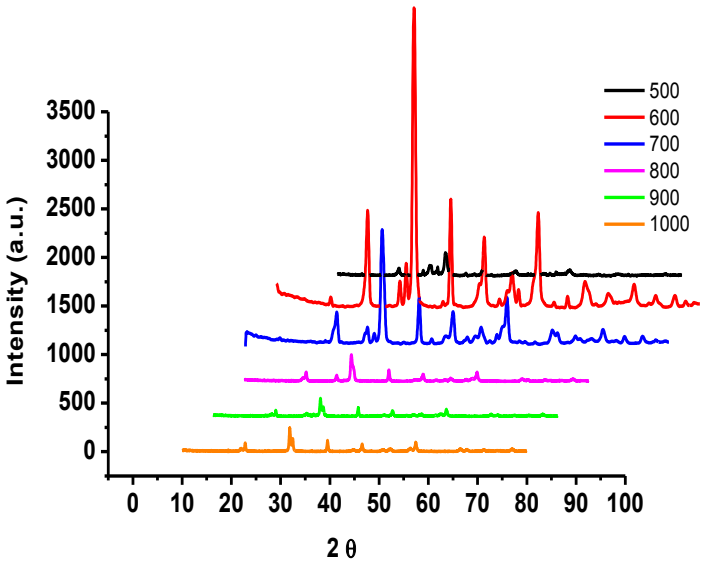


Fig. 2: X-ray diffraction pattern of PbTiO3 ceramics calcined at 500ºC to 1000ºC**.**

III.2. THERMAL ANALYSIS OF PT POWDER

Figure (3, 4) shows the thermo gravimetric analysis (TGA) and differential thermal analysis (DSC) of the PT powders carried out in Helium atmosphere with the heating rate of 20°C/min. TG curves exhibit three major losses; the first one located between 60 °C and 70 °C (of about 0.6459%) may be due to the elimination of water content from the prepared sample; the second occurring between 544.72°C and 635.94°C (of about 0.643%) due to the major decomposition reaction of organic compounds and the third one located between 828.74°C and 850 °C is due to removal of the combustion of residual carbon contents. The DSC curves are in conformity with these observations. There are two exothermic peaks in DSC curve at 64.13 °C to71.14 °C. The first one may be corresponding to the combustion of most of the organic species entrapped in PT polymerized gel such as citric acid and titanium (lV) isopropoxide. The second with a temperature range of 150 °C –550 °C is due to the decomposition of organic compounds and it indicates the beginning of crystallization of the perovskite phase.The red line of DSC curve represented the phase transition region of pbtio3 in 635°C . In other words this temperature represented Tc of PbTiO3 nano material.

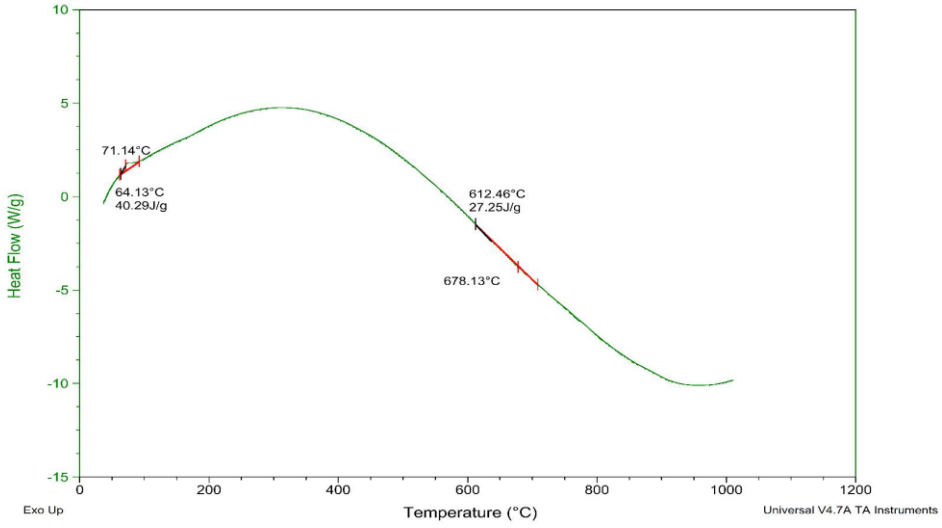


Fig.3: DSC curve for the PT powders synthesized by sol-gel method**.**

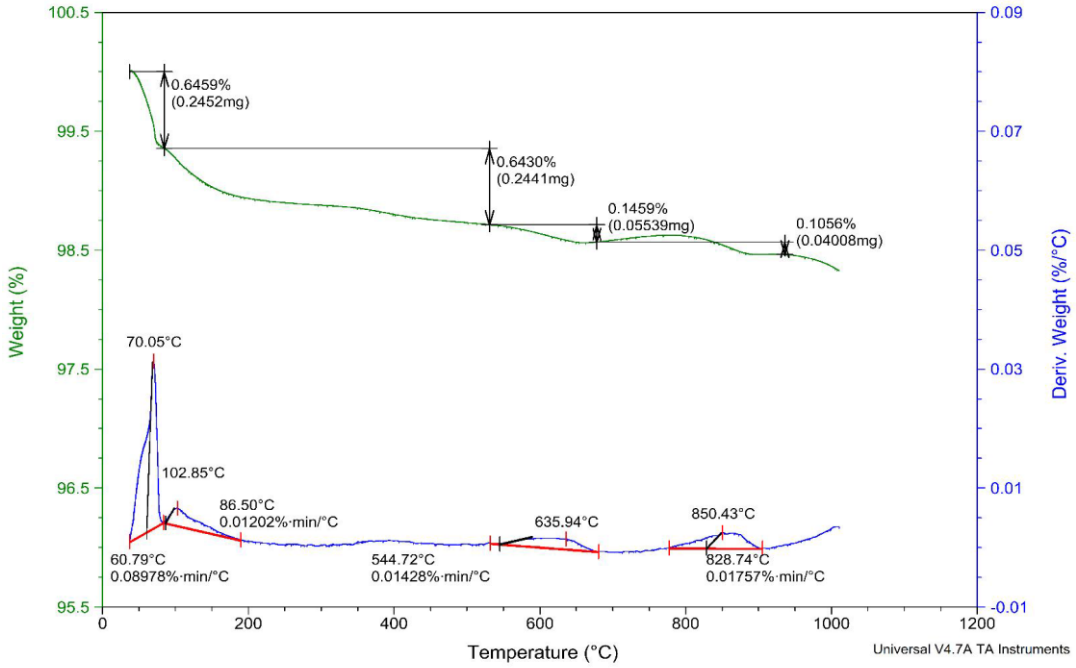
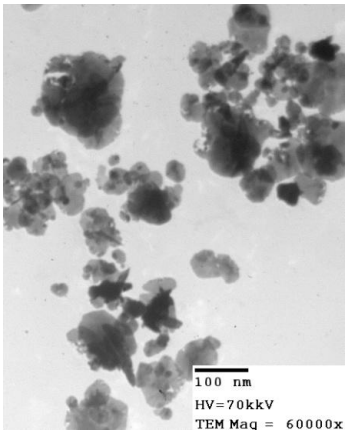


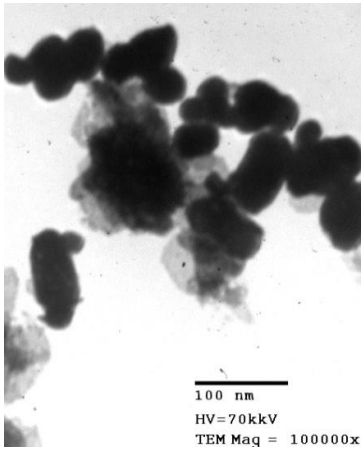
Fig.4: TGA curve for the PT powders synthesized by sol-gel route.

III.3. TEM ANALYSIS

Figure (5) a ,b ,c ,d ,e and f show the typical TEM image of the PT powder calcined at 500°C, 600°C, 700°C, 800°C, 900°C and 1000°C sintered 1100°C respectively. From TEM analysis, the primary particle size of the powder has been determined. The primary particle size of the PT powder has been found to be approximately in the range of 12–30 nm. From the TEM image, it is observed that the average size of the particle is around 12-18 nm and distribution of particle size of the powder is not uniform. It may be due to agglomeration of particles that resulted during the preparation the powder of $PbTiO_3$.



(a)



(b)

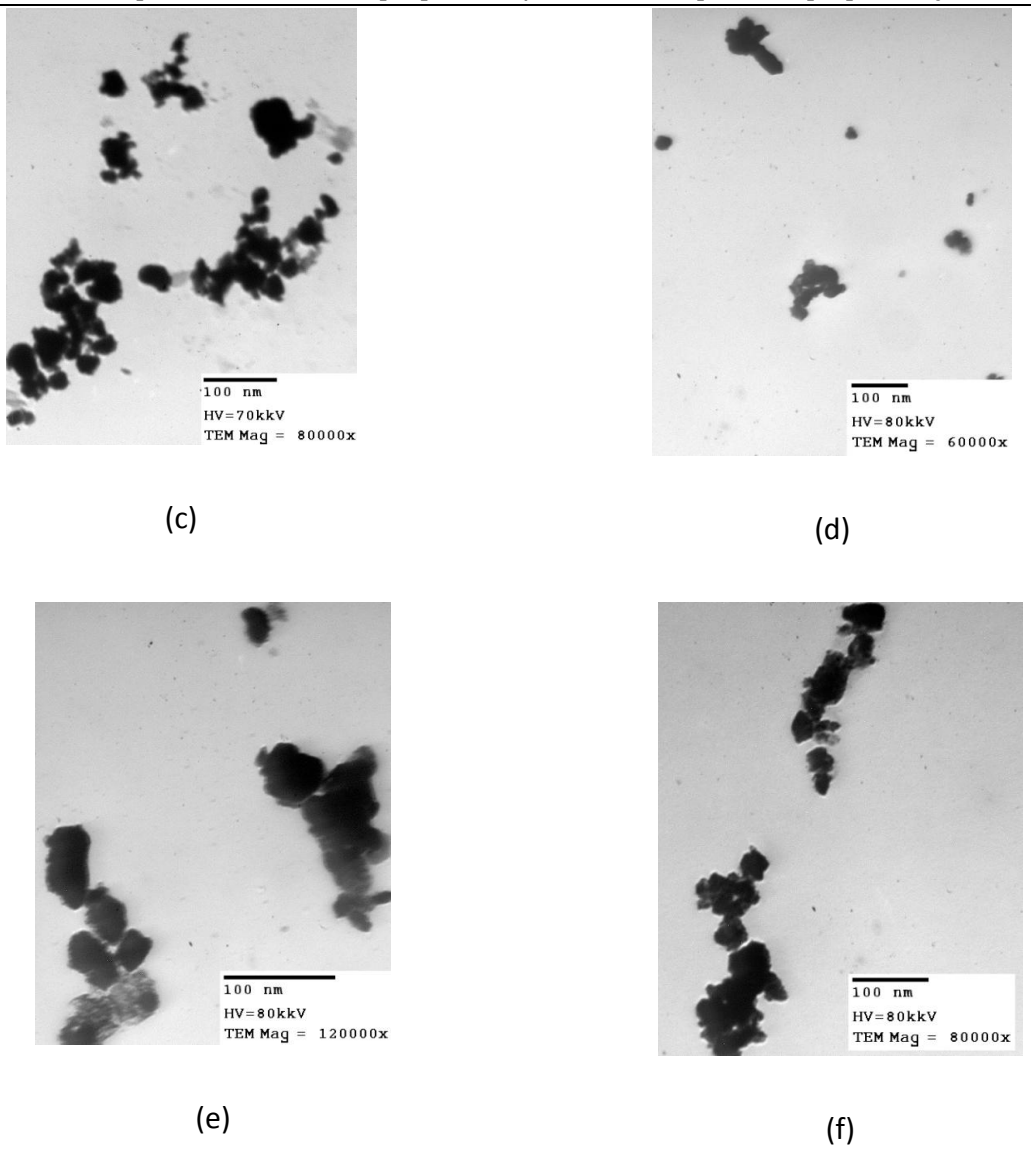


Fig. 5: TEM photographs of (a), (b), (c), (d), (e) and (f) represented the sample (Pb TiO3) Ceramics sintered (1100°c) are respectively.

III.4. OPTICAL PROPERTIES

The optical properties of the nanoparticles were studied by UV-Visible Spectrophotometer (UV-300II , TECHCOMP). . Figure 6 shows the room temperature UV-Vis Transmission spectrum of electrochemically synthesized in the 700 to 1100 nm wavelength range. The value of optical gap Eg is calculated using well known Tauc plot [18] is calculated by following equation:

$$h\nu\alpha = \left(h\nu - E_g^{opt}\right)^2$$

Where h is the Plank constant, ν is the frequency and is the optical band gap. Band gap energy of was calculated for the sample with at 1000 °C calcinations temperature .It give 2.6 eV as shown in figure 7 .

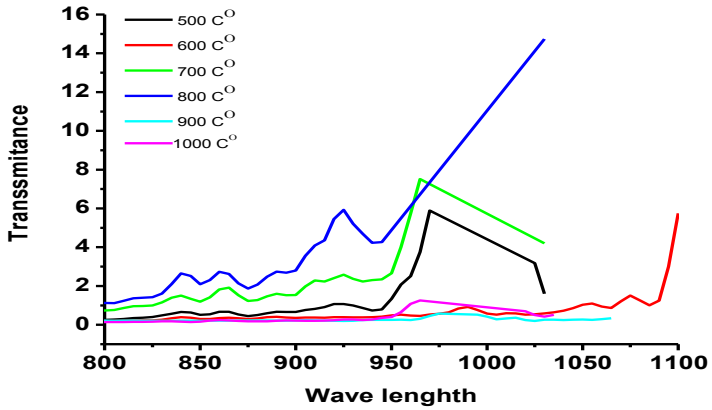


Fig. 6: Transmittance spectra of PT powders calcined for 2h at 500°C to 1000°C.

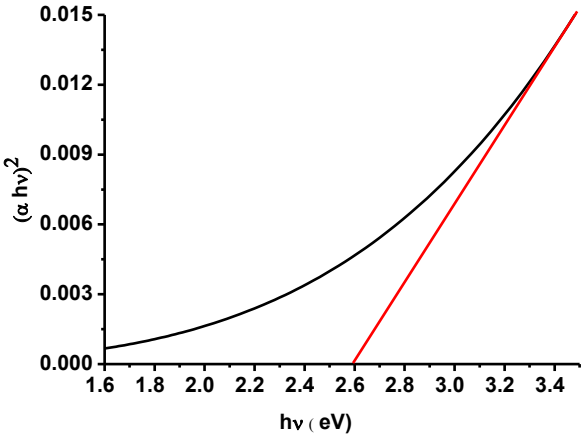


Fig. 7: Energy gap of PT powders calcined for 2h at 1000 °C.

III.5. SCANNING ELECTRON MICROSCOPE

In the present study, The scanning electron micrograph of the PbTiO3 samples calcined at 1000ºC and sintered at 1100°C for 2hr, as in Figure 8 shows surface of pellets the SEM micrograph was taken on the fractured surface of the sample using scanning electron microscope (SEM: JOEL JSM-5500 LV scanning microscope JEOL).The samples were made conducting by coating a thin layer of gold using a sputter coater. The shape of PbTiO3 domains are clear and shows 180° domain wall.

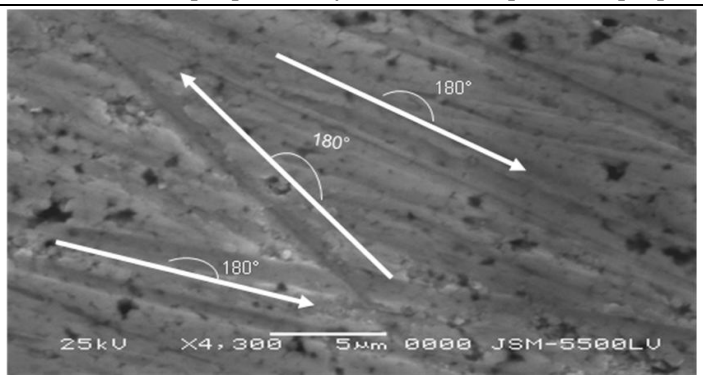


Fig. 8: SEM photographs of the sample PbTiO3 sintered at (1100°c).

III.6. DIELECTRIC PROPERTIES OF PT NANOPARTICLES.

Dielectric studies of the PT nano particles were carried out to analyses its response to an applied ac voltage (1V) as a function of both temperature and frequency. Figure 9 shows the dielectric constant (ε_r) of the PT ceramics as a function of temperatures for frequency 10k Hz at calcinations temperature 1000 °C. The dielectric constant (ε_r) increases gradually with rise in temperature and reached a maximum value εrmax at a particular temperature known as Curie temperature (Tc ~ 635 °C) . The maximum dielectric constant of $PbTiO_3$ powder calcined at 1000°C are about $312x10^2$,this value is higher than value of $PbTiO_3$ prepared by solid state method, means that the nano scale of PT particles changes the dielectric constant and Tc of $PbTiO_3$ to higher value as consider with we did not reach phase transition region.

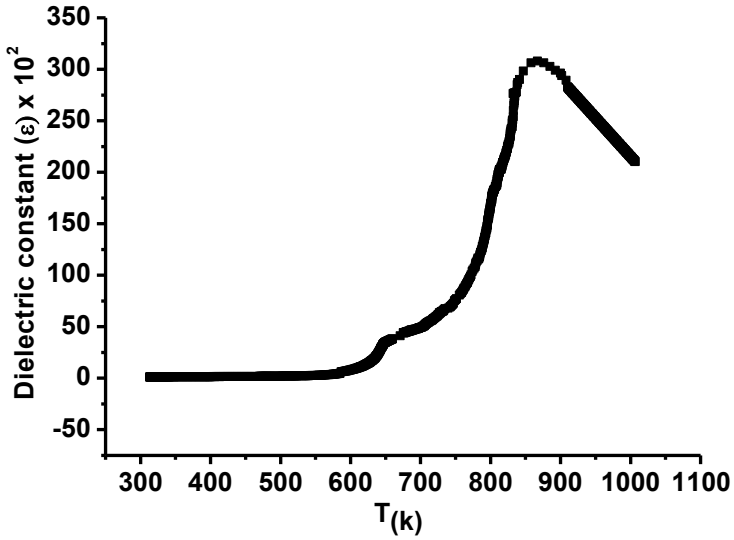


Fig. 9: Temperature dependence of the dielectric constant of PbTiO3 single phase calcined at 1000°C and annealed for 2 sintering at 1100°C

IV. CONCLUSION

$PbTiO_3$ nanoparticles have been successfully prepared by Sol-Gel method and its structural, optical properties and dielectric are been studied. From these studies it has been assessed that $PbTiO_3$ was successfully synthesized as nanoparticles at 1000 °C calcinations temperature for 2 hours. TEM analysis shows that the average grain size of pure PT powder about 12.49 nm. The SEM analysis clearly proved the presence of wall domains 180° .The energy gap reached the value equal to 2.6 eV. Dramatically change in the curie temperature (635 °C) happened and the maximum dielectric reached high value about (312).

V. ACKNOWLEDGEMENTS

Authors would like to thanks south valley University, Egypt, authority for providing funds under the University Research Project to carry out this work.

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