

Dielectric Studies of Lead Titanate Prepared by Wet Chemical Method

A. U. Bajpeyee, *N. V. Galande, S. H. Shamkuwar

Department of Physics, Smt. Narsamma Arts, Commerce and Science College, Kiran Nagar,
Amravati 444606, (M.S.) India.

Abstract:

Solution of molar proportion of precursors Lead Nitrate $[Pb(NO_3)_2]$, Titanium Isopropoxide $[C_{12}H_{28}O_4Ti]$ in liquid, and pure water stirred for 1 hr at $100^\circ C$ by using the wet chemical route. The white raw powder so obtained is then calcined at different temperature at $500^\circ C$, $550^\circ C$ and $600^\circ C$ for 4 hours. Thus obtained nanoparticles of Lead Titanate PT ($PbTiO_3$) were subjected to X-ray diffraction [XRD] studies. XRD of the lead titanate reveals 32.39 nm, 32.04 nm and 30.87 at $500^\circ C$, $550^\circ C$ and $600^\circ C$ calcinations.

Key words: Wet Chemical Route, $PbTiO_3$, XRD, Dielectric properties.

Date of Submission: 11-10-2021

Date of Acceptance: 25-10-2021

I. Introduction:

Perovskite systems (ABO_3) have been studied widely for its B site substitutions. Basically, $PbTiO_3$ has been considered to be one of the most important members of this family [1]. It has a high Curie temperature, high pyroelectric coefficient, low dielectric constant, and high spontaneous polarization. Lead titanate ($PbTiO_3$, PT) is a ferroelectric nanocrystalline powder that has not only been proved to be a technologically important material but also it is a significant component material in electronics such as capacitors, ultrasonic transducers, thermistors, and optoelectronics [2]. These systems are 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 [3-4]. Large c/a ratio in $PbTiO_3$ at low temperature confer tetragonal phase, it disintegrates into powder when cooled through the Curie point. Synthesis of $PbTiO_3$ by wet chemical methods offer advantages because of high-purity, good stoichiometry and controlled particle size [5-9].

The conventional solid-state reaction has a tendency to produce a coarse $PbTiO_3$ powder with compositional inhomogeneity and a degree of particle agglomeration if the processing parameters are not carefully optimized [10-14]. Therefore, many chemistry-based processing routes, including co-precipitation, sol-gel synthesis, hydrothermal and citrate routes have been devised for the preparation of an ultrafine, sintering-reactive $PbTiO_3$ powder. Our method of synthesizing $PbTiO_3$ relies on the reaction between Lead Nitrate $[Pb(NO_3)_2]$ and Titanium Isopropoxide $[C_{12}H_{28}O_4Ti]$ at high temperature [15-18].

Experimentation:

Molar proportions of $Pb(NO_3)_2$ (Lead Nitrate) is dissolved in Titanium Isopropoxide $[C_{12}H_{28}O_4Ti]$ in liquid. The lead titanate were prepared by dissolving solid lead nitrate powder in pure water and stirred for 1 hr at $100^\circ C$ in reaction flask, when the lead nitrate was dissolved in water, then a stoichiometric amount of titanium Isopropoxide was added to the solution and the solution was refluxed at $100^\circ C$ for 1 hr. and the solution was kept at $100^\circ C$ for 12 hr. to get nanocrystalline powder. Nanocrystalline powders with various crystallite sizes were obtained by calcining the powder at different temperatures at $500^\circ C$, $550^\circ C$ and $600^\circ C$ for 4 hr. Structure and phase transformation analyses were investigated by XRD in the range of 5° – 90° . The average crystallite size was calculated from the full width at half maximum of the diffraction lines using Scherrer's relation.

II. Results And Discussions

X-RAY DIFFRACTION:

XRD pattern of the $PbTiO_3$ calcined at $500^\circ C$, $550^\circ C$ and $600^\circ C$ is shown in Fig.1 at $500^\circ C$; the crystallization of tetragonal lead titanate phase began along with traces impurity phase. At $550^\circ C$ all peaks can be indexed to the $PbTiO_3$ with a tetragonal structure. No peak corresponding to any of the source materials or allotropic forms was found, suggesting that a pure crystalline compound exists. The crystallite size of the particles calcined at various temperatures could be calculated by the Scherrer's equation: $t = k\lambda/\beta\cos\theta$ (where t

is the average size of the particles, assuming particles are spherical, $k = 0.9$, λ is the wavelength of X-ray radiation, β is the full width at half maximum of the diffracted peak and θ is the angle of diffraction. The crystallite size obtained from XRD data at 500°C, 550°C and 600 °C were 32.39 nm, 32.04 nm and 30.87 nm respectively. The peak related to the plane 100 is getting suppressed with the elevated sintering temperature. This peak belongs to the excess amount of PbO present in the material. As sintering temperature is increased, the peak belonging to PbO is vanished and pure phase PbTiO₃ is obtained.

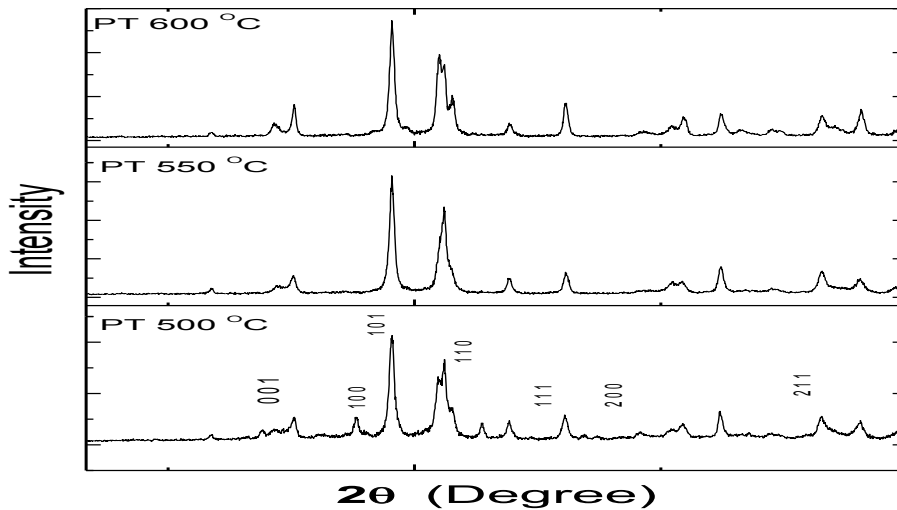


Fig. 1 XRD pattern

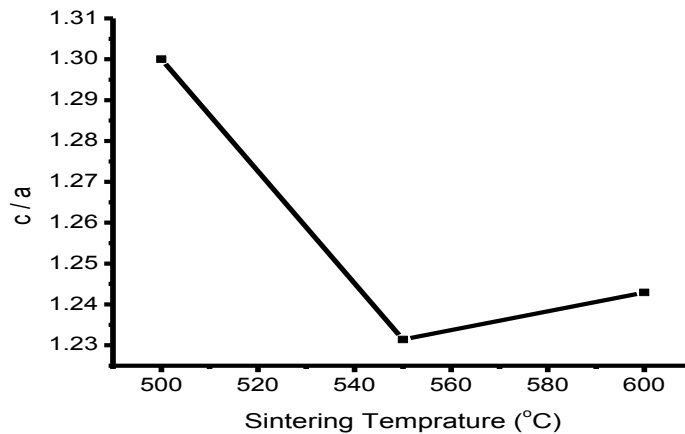


Fig.2 Sintering temperature vs. c/a ratio

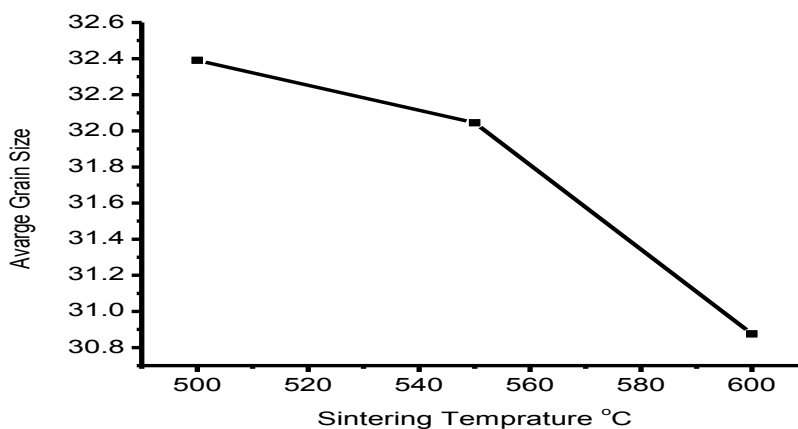


Fig.3 Sintering temperature vs. Average grain size

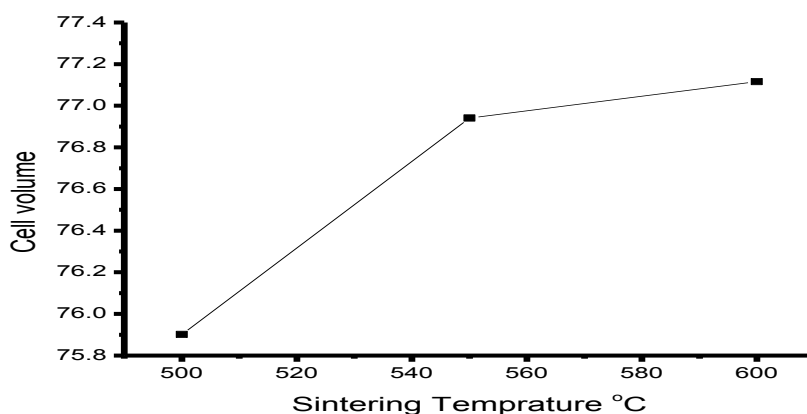


Fig.4 Sintering temperature vs. Cell volume

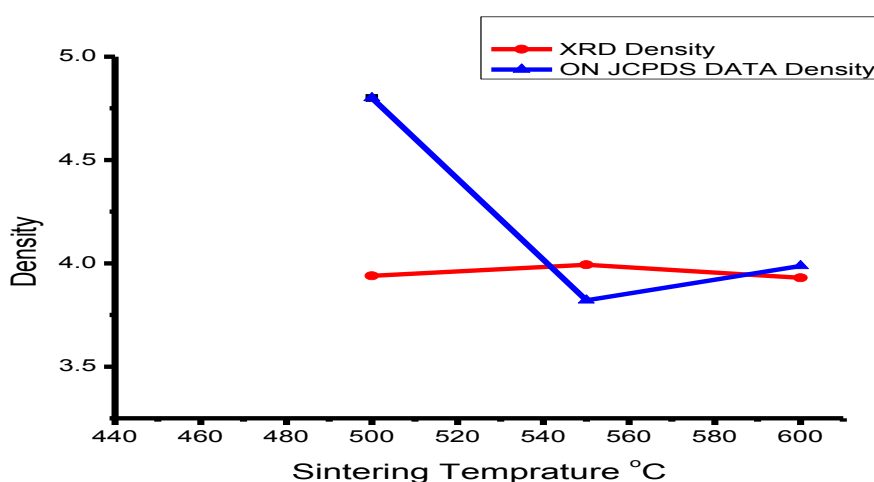


Fig.5 Sintering temperature vs. Density

Fig.2. shows the variation of c/a ratio with the sintering temperature, which clearly indicates c/a ratio, is maximum at 500°C which means stable tetragonal phase at 500°C and decreases for 550°C and 600°C. Decrease in c/a ratio afterwards indicates dispersion from tetragonality and an approach to the cubic phase with higher sintering temperature. Fig.3 shows the variation of average grain size with sintering temperature indicating decrease in average grain size with increasing sintering temperature. The cell volume increases with increasing sintering temperature. The density of the material is initially increases and then decreases slightly owing to the structural changes during calcinations. The change in the density is so small that it can be inferred that the density of the material is almost constant in the given calcinations temperature range.

Dielectric Properties:

The dielectrics properties of PT nanoparticles were studied to determine various electrical parameters with respect to frequency. Figure 6.shows the dielectric constant (k) of the PT nanocrystalline powders as a function of frequency at room temperature. The dielectric constant decreases with respect to frequency. The decrease in frequency is rapid in low frequency region and becoming constant in high frequency region representing dielectric dispersion. The dielectric dispersion with frequency shown by the material is due to Maxwell-Wagner type interfacial polarization. The large value of dielectric constant at low frequency is attributed to the presence of all types of polarization, whereas at higher frequencies the dominant contribution to dielectric constant is from electronic polarization only. Fig.6 shows variation of the dielectric constant with respect to calcinations temperature indicating that the charge holding capacity of the material decreases with increased calcinations temperature and this may be due to evaporation of oxide ions at higher calcinations temperature.

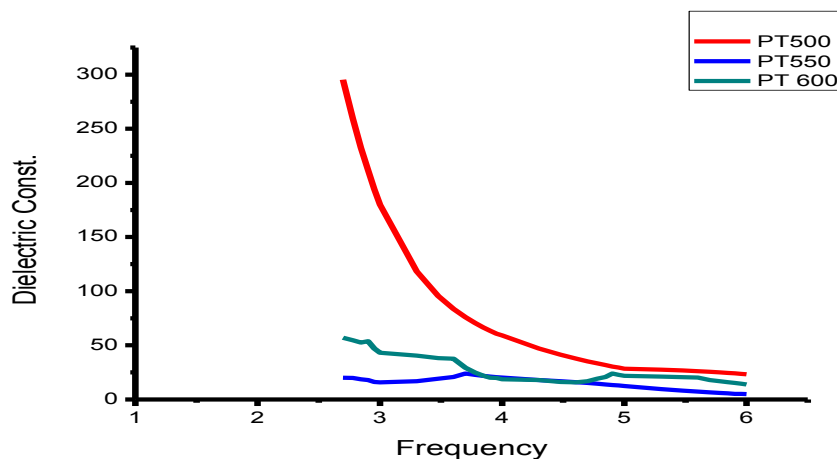


Fig.6 Frequency vs. Dielectric constant

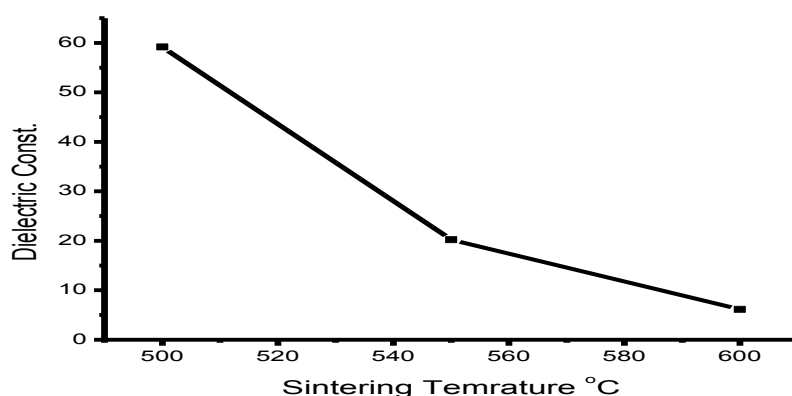


Fig.3 Sintering temperature vs. Dielectric constant

III. Conclusion:

This work done attempted to generalize the reaction for material synthesis by using the wet chemical route is successful. The average crystallite size 32.39 nm, 32.04 nm and 30.87 at 500°C, 550°C and 600°C calcinations was assured from XRD peaks. The variation in c/a ratio showed transition from tetragonal to Cubic phase. The grain size also decreases with increased calcinations temperature. Cell volume of the material increases with increased calcinations temperature. The Dielectric properties the large value of dielectric constant at low frequency attributed to the presence of all types of polarization, whereas at higher frequencies the dominant contribution to dielectric constant is from electronic polarization only. With increased sintering temperature, charge holding capacity of the material decreases owing to the evaporation of ions due to oxidation.

References:

- [1]. M.K.Gerges, Massaud Mostafa, Gehad M. Rashwan, Structural, optical and electrical properties of PbTiO₃ nanoparticles prepared by Sol-Gel method, International Journal of Latest Research in Engineering and Technology, Volume 2, PP 42-49, Issue 4 April 2016.
- [2]. D. Kapse, A. U. Bajpeyee, P. A. Murade Int Structural Properties of Lead Titanate Nanoparticles Prepared by Wet Chemical Route international journal of chem. Tech. Research. Vol.6 No.3, PP2096-2098 May-June 2014.
- [3]. Vijendra A. Chaudhari and Govind K. Bichile, Synthesis, Structural, and Electrical Properties of Pure PbTiO₃ Ferroelectric Nanocrystalline powders, Research Gate Hindawi Publishing Corporation Smart Materials Research Volume 2013, Article ID 147524, 9 pages May 2013.
- [4]. V. Chaudhari; G. K. Bichile, "Synthesis, Structural and Electrical Properties of Pure PbTiO₃ Ferroelectric Nanocrystalline powders"; Smart Materials Research, volume 2013, Pages 1-9.
- [5]. Bajpeyee A. U., Ph. D. Thesis "Structural and Electrical Studies of Dielectric Layers on Semiconductor" SGB Amravati University, Amravati (Maharashtra) India, 2012.
- [6]. A.Shukla and R. N. P. Choudhary, "Study of electrical properties of La₃₊/Mn₄₊ -modified PbTiO₃ nanonocrystalline powders"; Journal of Materials Science, Volume 47, issue 13 (2012) Pages 5074-5085.
- [7]. David N. Miller, John T.S. Irvine, "B-site doping of lanthanum strontium titanate for solid oxide fuel cell anodes"; Journal of Power Sources, Volume 196, Issue 17 (2011) Pages 7323-7.

- [8].) E. Perez-Delfin, J. E. García, D. A. Ochoa, R. Pérez, F. Guerrero, J. A. Eiras, "Effect of Mn-acceptor dopant on dielectric and piezoelectric responses of lead lanthanum zirconate titanate piezoceramics"; *Journal of Applied Physics*, Volume 110, Issue 3 (2011) Pages 34106-10.
- [9]. R.R. Doshi, P.S. Solanki, Uma Khachar, D.G. Kuberkar, P. S. R. Krishna, A. Banerjee, P. Chaddah, "First order paramagnetic-ferromagnetic phase transition in Tb³⁺ doped La_{0.5}Ca_{0.5}MnO₃ manganite"; *Physics B : condensed matter*, Volume 406, Issue 21, (2011) Pages 4031–4034.
- [10]. Emre Erdem, Peter Jakes, S. K. S. Parashar, Kamil Kiraz, Mehmet Somer, Andreas Rüdiger and Rüdiger-A Eichel, "Defect structure in aliovalently-doped and isovalently-substituted PbTiO₃ nano-powders"; *Journal of Physics: Condensed Matter* Volume 22 Number 34 (2010) Pages 345901-8.
- [11]. J. Ting and B. J. Kennedy, "Structure and Properties of Manganese-Substituted Bismuth Titanates"; *Journal of Physics: Conference Series*, Volume 251, Number 1 (2010) Pages 1-4.
- [12]. Xiaoping Dong, Minoru Osada, Hidekazu Ueda, Yasuo Ebina, Yoshinori Kotani, Kanta Ono, Shigenori Ueda, Keisuke Kobayashi, Kazunori Takada and Takayoshi Sasaki, "Synthesis of Mn-Substituted Titania Nanosheets and Ferromagnetic Thin Films with Controlled Doping"; *Chem. Mater.*, Volume 21 (19) (2009) Pages 4366–4373.
- [13]. Alejandro Ovalle, Juan Carlos Ruiz-Morales, Jesús Canales-Vázquez, David Marrero-López, John T.S. Irvine, "Mn-substituted titanates as efficient anodes for direct methane SOFCs"; *Solid State Ionics*, Volume 177, Issues 19–25 (2006) Pages 1997–2003.
- [14]. Arabjit Singh, O. P. Thakur, Chandra Prakash, K. K. Raina, "Structural and electrical properties of lanthanum-substituted lead titanate nanocrystalline powders, *Phase Transitions*"; *A Multinational Journal*, Volume 78, Issue 7-8 (2005) Pages 655-667.
- [15]. Jun Chen, Xianran Xing, Ranbo Yu and Guirong Liu, "Thermal Expansion Properties of Lanthanum-Substituted Lead Titanate Nanocrystalline powders"; *Journal of the American Nanocrystalline powder Society*, Volume 88, Issue 5 (2005) Pages 1356–1358.
- [16]. S. B. Majumder, R. S. Katiyar, F. A. Miranda, F. W. Van Keuls, "Improvement in electrical characteristics of graded manganese doped barium strontium titanate thin films"; *Applied Physics Letters*, Volume 82, Issue 12 (2003) Pages 1911-3.
- [17]. Jong-Jin Choi, Sang-Wook Kim and Hyoun-Ee Kim, "Effect of Manganese Ion Diffusion on the Microstructural Evolution of Lead Lanthanum Zirconate Titanate Nanocrystalline powder"; *Journal of the American Nanocrystalline powder Society*, Volume 85, Issue 3 (2002) Pages 733–735.
- [18]. S.B Majumder, M Jain, R.S Katiyar, "Investigations on the optical properties of sol-gel derived lanthanum doped lead titanate thin films"; *Thin Solid Films*, Volume 402, Issues 1–2 (2002) Pages 90–98.
- [19]. S. Bhaskar, S.B. Majumder, M. Jain, P.S. Dobal, R.S. Katiyar, "Studies on the structural, microstructural and optical properties of sol-gel derived lead lanthanum titanate thin films"; *Materials Science and Engineering: B*, Volume 87, Issue 2 (2001) Pages 178–190.
- [20]. Q. F. Zhou, H. L. W. Chan, Q. Q. Zhang, C. L. Choy, Raman spectra and structural phase transition in nanocrystalline lead lanthanum titanate, *Journal of Applied physics*, 15 JUNE 2001.
- [21]. Wenhua Jiang and Wenwu Cao, "Intrinsic and coupling-induced elastic nonlinearity of lanthanum-doped lead magnesium niobate-lead titanate electrostrictive nanocrystalline powder"; *Applied Physics Letters*, Volume 77 (2000) Pages 1387-1392.
- [22]. Hans Theo Langhammer, Thomas Müller, Karl-Heinz Felgner, Hans-Peter Abicht, "Crystal Structure and Related Properties of Manganese-Doped Barium Titanate Nanocrystalline powders"; *Journal of the American Nanocrystalline powder Society*, Volume 83, Issue 3 (2000) pages 605-11.
- [23]. S. B. Majumder, S. Bhaskar, P. S. Dobal & R. S. Katiyar, "Investigations on sol-gel derived lanthanum doped lead titanate (PLT) films"; *Integrated Ferroelectrics: An International Journal*, Volume 23, Issue 1-4 (1999) pages 127-148.
- [24]. P. S. Pizani, J. A. Eiras, "Short-range disorder in lanthanum-doped lead titanate nanocrystalline powders probed by Raman scattering"; *Applied Physics Letters*, Volume 72, Issue 8 (1998) pages 897-899.
- [25]. G. A. Rossetti Jr, L. E. Cross, J. P. Cline, "Structural aspects of the ferroelectric phase transition in lanthanum-substituted lead titanate"; *Journal of Materials Science*, Volume 30, Issue 1 (1995) pages 24-34.
- [26]. C. Sudhama, J. Kim, J. Lee, V. Chikarmane, W. Shepherd and E. R. Myers, "Effect of lanthanum doping on the electrical properties of sol-gel derived ferroelectric lead-zirconate-titanate for ultra-large-scale integration dynamic random access memory applications"; *J. Vac. Sci. Technol.*, B 11, issue 4 (1993) pages 1302-9.

A. U. Bajpeyee, et. al. "Dielectric Studies of Lead Titanate Prepared by Wet Chemical Method." *IOSR Journal of Applied Physics (IOSR-JAP)*, 13(5), 2021, pp. 14-18.