Available online at www.derpharmachemica.com



Scholars Research Library

Der Pharma Chemica, 2015, 7(10):175-185 (http://derpharmachemica.com/archive.html)



ISSN 0975-413X CODEN (USA): PCHHAX

Dielectric and electrical properties of lead zirconate titanate

R. Balusamy^a, P. Kumaravel^b and N. G. Renganathan^{c*}

^aDepartment of Mechanical Engineering, Al-Ameen Engineering College, Erode ^bDepartment of Mechanical Engineering, Institute of Road and Transport Technology, Erode ^c School of Basic Sciences, Vel Tech University, Chennai

ABSTRACT

Lead zirconate titanate (PZT) $(P_bZ_rO_3 - P_bT_iO_3)$ were prepared by mixed oxide method at 1100°C. Crystalline nature of the synthesized PZT has been confirmed by X-ray powder diffraction studies. The particle size and strain is calculated from X-ray peak broadening analysis by using Williamson-Hall plot. The crystallite size is also calculated using Debye-Scherrer's formula. Also, the surface morphology and particle size of the samples were imaged using scanning electron microscopy (SEM). Dielectric measurement demonstrates that decrease in dielectric constant with increase in temperature. The temperature dependence of the ac conductivity indicated that the conduction process is due to singly ionized (in ferroelectric region) and doubly ionized (in paraelectric region).

Key words: PZT ceramics, dielectric spectroscopy, dielectric losses, SEM.

INTRODUCTION

Lead zirconate titanate (PZT) – a ferroelectric ceramic material has piezoelectric properties and reciprocal behavior. This material is used to convert electrical energy into mechanical energy and vice-versa. The material properties of PZT have been the subject for significant research in recent years due to its excellent applications in microelectromechanical (MEMS) and nano-electromechanical (NEMS) devices. Since it is a potential candidate for sensor applications the material needs further research. Micro and nano sensors are precisely calibrated to work within a set range of specifications. It is a well known ferroelectric material and it has wide application as such as transducers, actuators, sensors and motors. Because of its high density, low hydrostatic piezoelectric coefficients of charge and voltage it is useful for hydrophones and ultrasonic devices. It has been focused on composite fabrication of PZT based piezoelectric materials for sensing and actuating. PZT is also used in the manufacture of ceramic resonators for reference timing in electronic circuitry. Being pyroelectric, this material develops a voltage difference across two of its faces when it experiences a temperature change. As a result, it can be used as a heat sensor. Prior to sol gel processing techniques, PZT films were prepared using more costly and intensive techniques such as RF sputtering, electron beam evaporation, and ion beam deposition [1]. Commercially used PZT ceramics are always modified by different dopants and are divided into the "soft" (donor doped) and "hard" (acceptor doped) groups which are normally prepared by substituting the A-site or B-site ions with donor and acceptor dopants, respectively [2]. Compared with the undoped composition, hard PZT shows lower permittivity, piezoelectric coefficients and elastic compliances, low dielectric and mechanical losses, lowered resistivity, pronounced ageing, and pinched ferroelectric hysteresis in aged state. In contrast, soft PZT shows higher properties, larger losses, improved resistivity, low ageing, square polarization loops, easy poling and depoling [3,4]. Electrical properties of PZT ceramics were determined by many researchers. Piezoelectric and magnetic properties of PZT composite were studied by Hsien-Kuang Liu etal. [5]. The optical characterization of PZT prepared by sol-gel method indicates that band gap decreases with increase in temperature [6]. Qun Guan has given the vibrational analysis of spherical symmetry problems in piezoelectric and piezomagnetic materials [7]. Ernst Gunter Lierke etal has given the various aspects of the possible applications of piezoelectric composite material as actuators, motors and transducers [8]. Structural, dielectric and electrical properties of lead zirconate titatanate and CaCu₃Ti₄O₁₂ ceramic composite has been reported by Arun Chamola etal [9]. The influence of grain size on the intrinsic and extrinsic elastic dielectric properties of a ferroelectric PZT system was studied by Clive A. Randall, et al [10]. PZT ceramic fibers prepared by sol-gel route when heat treated at 1000°C had ferroelectric property and showed square-shaped hysteresis loop with the remnant polarization (Pr) of 25µC/cm2 and coercive field (Ec) of 9kV/cm. [11]. Piezoelectric and dielectric reliability of lead zirconate titanate thin films was studied by Ronald G. Polcawich et al. and they showed excellent reliability, with 99% of the devices surviving to 109 cycles under uni polar drive [12]. In the present work, we are reporting the synthesis of Lead zirconate titanate $(P_b Z_r O_3 - P_b T_i O_3)$ (52/48) by mixed oxide method. The synthesized powders were characterized by powder X-ray diffraction (XRD) and scanning electron microscope. The thermal and dielectric properties have also been discussed in detail in this communication. The electrical properties have also been discussed in detail.

MATERIALS AND METHODS

Mixed oxide method was used to obtain piezoelectric material (Lead zirconate $P_bZ_rO_3$ and Lead titanate $P_bT_iO_3$) of composition (52/48) respectively. Oxide powders (PbO, ZrO₂ and TiO₂) with high purity were used as raw materials to synthesize PZT ceramics. For lead zirconate 33.5% of lead oxide and 18.5% of zirconium oxide are taken. Similarly for lead titanate 35.35% of lead oxide and 12.65% of titanium oxide was taken. These two powders are mixed in a ball mill for 48 hours. The powder is hot pressed at 25 to 120 MPa slowly at a heating rate of 20^0 C /min and the final temperature is 800^0 C. The preparation of PZT is shown in the Fig.1 as a flow chart.

Characterization of PZT

X-ray powder diffraction data of PZT were collected at room temperature using Rich Seifert X-ray powder Diffractometer with CuKa radiation ($\lambda = 1.5406$ Å) in the 20 range from 10 to 70° at a scanning rate of 1 min⁻¹. The morphology and microstructure of as-prepared PZT was observed by a scanning electron microscope (JEOL JSM 6460 LV). Thermal gravimetric analysis (TGA) and differential temperature analysis (DTA) were employed to determine the thermal stability and complete formation of the synthesized PZT compound. The thermal behavior of PZT was studied at 20°Cmin⁻¹ by using a SDT Q 600 V 8.2 Built 95 thermal analyzer. The experimental conditions were: (a) continuous heating from room temperature to 800°C for 20°Cmin⁻¹.; (b) Nitrogen gas dynamic atmosphere (90cm³min⁻¹); (c) alumina, crucible; (d) sample of mass: 3.6120 mg for 20°Cmin⁻¹. PZT was subjected to dielectric studies using a HIOKI model 3532-50 LCR HITESTER with a conventional two terminal sample holder. The sample was electrode on either side with air-drying silver paste so that it behaves like a parallel capacitor. The studies were carried out from 313K to 373 K for frequency varying from 50Hz to 5 MHz.

RESULTS AND DISCUSSION

4.1 Structural analysis

X-ray powder diffraction analysis is used to check the crystalline purity of synthesized PZT compound. Fig.2 shows the powder X-ray diffraction of synthesized PZT. The studies on crystalline materials require an accurate determination of crystallite size as well as the micro strain induced in the material. X-ray diffraction (XRD) is a well known technique for this purpose. Based on XRD principles, numerous approaches such as the use of Scherrer equation, integral breadth analysis, single line approximation, Hall Williamson method, Rietveld refinement method etc. have been developed for the crystallite size determination. The average particle size (d) is estimated from the broadening of the X-ray diffraction peaks from Scherrer's equation. The maximum intensity peak occurs at 2θ =55°. The average crystallite size calculated from Scherrer's formula is found to be 17.35 nm. The shift in X-ray diffraction peak position can also occur from the strain induced in the unit cell and this effect of strain can be obtained from the intercept at the Y axis (22.1nm) and the slope (0.16027) respectively. The shift in X-ray diffraction peak position can also occur from the strain induced in the unit cell. This effect of strain can be investigated using Williamson–Hall plot. The particle size and strain can be obtained from the intercept at the Y axis (22.1nm) and the slope (0.16027) respectively. The shift in X-ray diffraction peak position can also occur from the strain induced in the unit cell. This effect of strain can be investigated using Williamson–Hall plot. The particle size and strain can be obtained from the intercept at the Y-axis and the slope, respectively.

N. G. Renganathan et al

The crystallite size (D) of PZT was determined by Debye-Scherrer's formula using equation

 $D = K\lambda / (\beta_{1/2} \cos \theta) \tag{1}$

where K=0.89; λ =1.5405A° and $\beta_{1/2}$ is the peak width of the reflection at half intensity. As the powder sample was used for XRD, the effect of the strain, instruments and other unknown factor causing the broadening of the peak were ignored. The average value of the crystallite size of PZT is found to be 17.35µm.

4.2 Surface morphology

The scanning electron microscopy (SEM) is a useful technique to study the topography, morphology and composition of the materials with much higher resolution. Micro structural features such as grain size, grain boundary, and pores were characterized by means of scanning electron microscopy (SEM). When a beam of highly energetic electrons strikes the sample, the secondary electrons, X-rays and back-scattered electrons are ejected from the sample. The samples used for SEM observation were polished down to optical quality. Depending on the samples, different etching methods were used to reveal grain boundaries. For soft PZT ceramic samples, grain boundaries in good contrast were observed after thermal etching at 1050°C for 30 minutes in air. Before the SEM observation, a layer of gold (about 20 nm) was deposited on the etched surface by sputtering to avoid the electron accumulation on the sample surface. A JEOL JSM 6460 LV scanning electron microscopy was used to conduct the observations. Figure 4 shows the typical SEM image of the PZT powder. From SEM analysis, the primary particle size of the powder has been determined and it is found to be in the range of 1µm-500nm. The distribution of the particle size of the pellet is not uniform, and it may be due to agglomeration of particles that resulted during the preparation of pellet. It is observed that the samples are uniform and the grains are in the order of micrometers. It can be noticed that the samples are uniform and the grains are in order of micron size. These micrographs revealed that the grain structure of the samples is dense, crack free and smooth [5,13]. The micrographs indicate the existence of uniform microstructure in the materials. The grains of equal sizes appear to be distributed homogeneously throughout the surface of the samples. It can notice that the samples are uniform and the grains are in order of micron size.

4.3 Dielectric studies

The dielectric analysis is an important characteristic that can be used to fetch knowledge based on the electrical properties of a material medium as a function of temperature and frequency. Based on this analysis, the capability of storing electric charges by the material and capability of transferring the electric charge can be assessed.

The dielectric constant is calculated using the formula $\epsilon' = Ct/\epsilon oA$ (2)

where *C* is capacitance (F), *t* the thickness (m), *A* the area (m2), and εo the absolute permittivity in the free space having a value of 8.854 *10⁻¹² Fm⁻¹.

For a dielectric characterization, PZT crystals are ground well to get powdered sample. Then the powdered PZT was pressed well under high pressure and made into a pellet of dimension of having diameter 7.41mm length; 3.37mm breadth; thickness 3.15 mm. The surface of the sample was coated with silver paste which acts as electrodes. The experiment was carried out from 50Hz to 5MHz for different temperatures varying from 313-353K. Fig. 5 and 6 show the variation of dielectric constant and dielectric loss with respect to various frequencies ranging from 100 Hz to 5 MHz. It has been observed that the dielectric constant decreases with the increasing in frequency. The high value of dielectric constant at low frequencies may be due to the excitation of bound electrons, lattice vibrations, dipole orientation and space polarizations. It is a typical characteristic of dielectric/ferroelectric materials. The fall in dielectric constant arises from the fact that polarization does not occur instantaneously with the application of electric field because of inertia. At low frequencies, all polarizations (electronic, ionic, orientation and space charge) contribute [14]. The larger value of dielectric constant and dielectric loss at low frequency arises due to the presence of space charge polarization near the grain boundary interfaces, which depends on the purity and perfection of the sample [15]. Non switching linear responses in the dielectric graphs are ascribed to space charge polarization. The dielectric constant was almost constant upto 250 ° C. Then ε increases gradually and attains a maximum value at Curie Temperature. After T_c it decreases. This dielectric analysis indicates a phase transition and this may be due to ferroelectric to para electric phase. The T_c (Curie Temperature) of pure PZT is 350 to 370 ° C which is seen from the dielectric constant temperature graph. But the dielectric peaks are broadened and this may be due to the characteristic behavior of disordered perovskite structure with diffuse phase transition. From the graph of the loss of tangent which increases with increasing frequency it is clear that conductivity increases and above 300° c is observed. This increase in the conductivity is attributed to the increase in polarizability of the materials around 300 to 400° C where T_c lies. But at higher temperature beyond T_c a transformation occurs from piezoelectric phase to non piezo electric phase. Undoped PZT, as in the present case, possesses p type conductivity (hole type semiconductor) and this occurs because of lead oxide evaporation from PZT during the formation stage. And due to this space charge both centers of negative charges and whole carriers increase dramatically and these causes an internal field inside the grains of PZT and this field may inhibit domain motion. This inhibition of domain motion reduces the dielectric loss and this is reflected in the dielectric loss vs Temperature graph.

As frequency increases, the polarization with large relaxation times cease to respond and hence the decrease in dielectric constant. The same type of frequency-dependent dielectric behavior is found in ferroelectric ceramics [16]. When the frequency is increased, the orientation polarization decreases since it takes more time than electronic and ionic polarization. This decreases the value of relative dielectric constant ε reaching a constant value at higher frequency correspondingly to interfacial polarization. On the other hand the dielectric constant with temperature can be attributed to the fact that the orientation polarization is connected with thermal motion of molecules so dipole cannot orient themselves at low temperatures. When the temperature is increased the orientation of the dipole is facilitated and thus increases the orientational polarization which leads to increases of the dielectric constant with temperature. However after a certain temperature the thermal energy is very high to restrict the polarization which leads to the disordered state (paraelectric). Hence, we have observed a transition from ferroelectric to paraelectric phase with the temperature.

Fig. 7. Shows the temperature dependence of dielectric constant (ϵ) at five different frequencies ranging from 100Hz to 5MHz. Transition is seen at higher frequencies. The dielectric constant was almost constant up to 330°C, then ϵ increases gradually attaining a maximum value of ϵ at Curie temperature and thereafter it decreases with further increase in temperature. This indicates a phase transition from ferroelectric to paraelectric phase at that particular temperature called Curie temperature (T_c). The dielectric peaks are broadened rather than a sharp peak (as in normal ferroelectrics) around T_c, which is one of the characteristic of disordered perovskite structure with diffuse phase transition. This broadening is due to the composition fluctuation [17] or substitution disordering in the arrangement of cation in one or more crystallographic sites [18] in the structure leading to a microscopic heterogeneity in the composition and thus in a distribution of different local Curie points. The temperature dependence of tangent loss (tan\delta) of PZT with selected frequencies (1,10,100 KHz and 1,5MHz) is shown in Fig.8. It was observed that tangent loss is constant upto transition temperature and then increases to a maximum value due to space charge polarization and again decreases with increasing temperature [18, 19, 20]

Fig.9 and 10 give the variation in resistivity and conductivity with the frequency for PZT. The a.c resistivity and A.C. conductivity was calculated using the following relation:

 $\begin{array}{l} P = A/2\pi \, fCd \\ \sigma\rho = 1 \; /\rho \end{array}$

where C is the capacitance, d is the thickness, A is the area of the crystal, and f is the frequency of the applied field. It is seen in Figure 10 that A.C. resistivity decreased rapidly as frequency increased. Obviously reverse trend was observed for a.c conductivity (Fig. 10) for PZT material [21].

4.4 Impedance spectral analysis

Fig.11 show the complex impedance spectrum (Z' Vs Z" called Nyquist plot) of PZT ceramic measured at different temperatures as a function of frequency. The effect of temperature on impedance behavior of the material sample is clear shown with rise in temperature. The impedance spectrum is characterized by the appearance of semicircular arcs. This pattern of arcs changes with rise in temperature and this is indicated in the figure. Each semicircular arc in the impedance pattern may be attributed to a parallel combination of resistance and capacitance. The arcs are becoming semicircular with increase of temperature. The arcs are moving closer to the origin with increase of temperature. A single semicircular arc in the complex impedance diagram indicates that the materials have electrical conduction only from the grains and not from the grain boundaries. The shift in the arc towards origin as temperature increases in the complex plane diagram indicates the resistive behavior of the sample which may be due to the conduction taking place due to grain boundary. At low frequencies dispersion occur (not shown) due to

N. G. Renganathan *et al*

polarization. At higher frequencies it becomes almost independent of both frequency and temperature. Similar variations of imaginary part of impedance with frequencies at lower temperature occur and this may be due to increase in a.c conductivity with temperature. At higher frequencies the imaginary part of impedance exhibits peaks and these peaks shift towards higher frequencies with increasing temperature and this occurs in a broadening manner with a decrease in peak height. This may be due to thermally activated dielectric relaxation process in the materials and this may be due to reduction in the bulk resistance with temperature.



Figure 1. Flow chart for synthesis of PZT



Figure 2 X-ray powder diffraction pattern of PZT



Figure 3. W-H plot PZT

www.scholarsresearchlibrary.com

N. G. Renganathan et al



Fig.4 SEM images of PZT



Fig.5 Dielectric constant Vs Log F



Fig.6. Dielectric loss Vs Log F



Fig.7. Dielectric constant Vs temperature

www.scholarsresearchlibrary.com



Fig.8. Dielectric loss Vs Temperature



Fig.9.. Resistivity Vs Log F







Fig.11 Nyquist plot of PZT

www.scholarsresearchlibrary.com

CONCLUSION

In the present work, we have prepared Lead Zirconate titanate (PZT) ($P_bZ_rO_3$ - $P_bT_iO_3$) with composition by mixed oxide method. From SEM analysis, the primary particle size of the powder has been determined and it is found to be in the range of 1µm-500nm. X- ray diffraction pattern shows the crystalline nature of PZT. The average value of the crystallite size of PZT is found to be 17.35µm. Thermal studies show that the synthesized PZT is thermally stable up to 360°C. Dielectric measurement demonstrates that decrease in dielectric constant with increase in temperature. The temperature dependence of the ac conductivity indicated that the conduction process is due to singly ionized (in ferroelectric region) and doubly ionized (in paraelectric region).

REFERENCES

[1] Yi, G., Sayer, M. 1996. Journal of Sol-Gel Science and Technology 6:65-74.

[2] B. Jaffe, W. R. Cook, and H. Jaffe, Piezoelectric ceramics. New York: Academic Press, 1971.

[3] M. I. Morozov and D. Damjanovic, Journal of Applied Physics, vol. 104, no. 3, p. 034107, 2008.

[4] M. I. Morozov and D. Damjanovic, Journal of Applied Physics, vol. 107, no. 3, p. 034106, 2010.

[5] Hsien-Kuang Liu, Jin H.Huang, Journal of Materials Science 40 (2005) 1975-1985

[6] M.Prabhu, I.B.Shameem Banu, S.Gopalakrishnan, Murthy Chavali, S.Umapathy, Adv.Sci.Eng.Med.2013, 5; 1-4

[7] Qun Guan, vibration analysis of the piezoelectric and piezomagnetic materials in spherical symmetry, communications in Control Science and Engineering CCSE vol. 1 (1) **2013**; 1-6

[8] Ernst Gunter Lierke, Water Litimann, Takeshi Morita, Tobias Hemsel, J. of the Korean Physical Society, 57, 4, 2010, 933-937

[9] Arun Chamola, Hemant Singh, U.C.Naithani, Shubhash Sharma, Uday Prabhat, Pratiksha Devi, Anuradha Malik, Alok Srivastava, R.K.Sharma, *Adv. Mat.Lett.* **2011**, 2(1) 26-31.

[10] Clive A. Randall, Namchul Kim, John-Paul Kucera, Wenwu Cao, and Thomas R. Shrout; J. Am. Ceram. Soc., 81 [3] 677–88 (1998)

[11] Manfang MAI, Cheng LIN, Zhaoxian XIONG, Hao XUE and Lifu CHEN; Journal of Physics: Conference Series 152 (2009) 012077; doi:10.1088/1742-6596/152/1/012077

[12] Ronald G. Polcawich and Susan Trolier-McKinstry; J. Mater. Res., Vol. 15, No. 11, Nov 2000; 2505-2513.

[13] D. Viehland, S. J. Jang, L. E. Cross, M. Wuttig, Phys. Rev. B 46 (1992) 8003.

[14] M. Meena and C. K. Mahadevan, Crystal Research and Technology, vol. 43, no. 2, pp. 166–172, 2008.

[15] S. Aruna, G. Bhagavannarayana, M. Palanisamy, P. C. Thomas, B. Varghese, and P. Sagayaraj, *Journal of Crystal Growth*, vol. 300, no. 2, pp. 403–408, **2007**

[16] R. Lal, S. C. Sharma, R. Dayal, Ferroelectrics. 100 (1989) 43.

[17] Smolensikii GA, J.Phys.Soc. Japan 1970, 28,26

[18] Lines ME, Glass AM, in principles and applications of ferroelectrics and related materials, Oxford Univ. Press, Oxford **1977**

[19] Rajan R, Kumar R, Behera B, Choudhary RNP, Materials Chemistry and Physics 2009, 115, 473.

[20] N. Kanagathara, G. Anbalagan, *International Journal of Optics* Volume **2012**, Article ID 826763, 6 pages doi:10.1155/2012/826763

[21] N. Pattanaboonmee, P. Ramasamy, R. Yimnirun, and P. Manyum, "A comparative study on pure, l-arginine and glycine doped ammonium dihydrogen orthophosphate single crystals grown by slow solvent evaporation and temperaturegradient method," *Journal of Crystal Growth*, **2010**.