The Effect of Sintering Temperature on the Electrical Properties and Particle Size of the Compound Ferroelectric PZT Prepared by Wet Chemical Methods

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Abstract

Lead Zirconate Titanate (PZT) nanopowder of ratio 35/65 (Pb(Zr0.35Ti0.65)O3 is prepared by one of the most wet-chemical routes called Sol-Gel Processing Method. The Lead Zirconate Titanate (PZT) is prepared from Lead Acetate and Zirconate (IV) isopropoxide as a source of metals. The acetic acid can be used as a solvent, and 2-methoxy was used as a stabilizer for Titanate (IV) isoproxide. The heat-treated powders at different sintering temperatures are characterized using the XRD diffraction technique, SEM, and LCR meter. XRD pattern shows the tetragonal phase of 35/65 Zr/Ti composition. They exhibited high density which is slightly different from the theoretical density, decrease of voids, stoichiometric chemical material, and homogeneity from both physical and chemical material. It has been found that each ceramic sample was exhibited different particles size depending on sintering temperature. The present work is well-crystallized with nanoparticles and single-phase perovskite PZT powders that can be obtained after heat treatment above 550°C for two hours. The dependence of this crystallization temperature is observed on the preparation condition. Lattice constant distortion is realized on dielectric constant, especially on the tetragonal phase.

Keywords: piezoceramics materials, sol-gel, PZT, Curie temperature, dielectric properties

1. Introduction

The ferroelectric materials studied during the last 20 years belong to their excellent physical properties, which make them promissory materials for technological applications [1]. Potassium dihydrogen phosphate (K2H2PO4), Barium Titanate (BaTiO3), Lithium niobate (LiNbO3), Rochell salt (NaK4C4H4O6.4H2O), Rochell salt (NaK4C4H4O6.4H2O) and potassium nitrate (KNO3) can be defined as ferroelectric materials[2]. Reference to this, History displays a continuous succession of new materials from various ceramics formulations, their forms (bulk, films) fabrication techniques as well as functional properties among the perovskite oxide such as Pb(Zr, Ti)O3, BaTiO3, BaSrTiO3, have dominated the field[3].
The best ferroelectric materials regarded to date for various application is lead Zirconate Titanate (Pb(Zr, TiO₃). Most electronic devices such as modulators, ferroelectric memories, actuators, optical fibers, and sensors have used the PZT ceramics compound [4]. A sol-gel method, mixed oxide, drying hydrothermal, solid-state reaction, and sputtering spray are methods of preparation of PZT[5].

The solid-state reaction process used to prepare PZT powders by oxides as starting raw materials[6]. It requires high temperature may lead to loss of Lead Oxide, which in turn affects the poor performance of PZT ceramics.

Along with, during the milling, impurity introduces large particle size, and inhomogeneity disadvantaged for solid-state reaction method which in turn degrades the performance of final PZT performance[7]. So many wet chemical routs discovered to prepare good quality PZT powders such as sol-gel, hydrothermal, and another chemical process. The sol-gel method is a particular interest that produced high purity ultrafine nanopowders[8].

Regarding the disadvantages of wet-chemical routes, for instance, it is challenging to avoid the formation of intermediate phases during the drying or calcination process. “One major problem of the sol-gel process is that it does not provide desired perovskite phases” directly but will get it after some stage such as calcination: [5, 7].

Besides, the method of synthesis with high-quality PZT powders plays a significant role to get the desired properties of PZT ceramics. PZT ceramics performance depends on particle size, chemical homogeneity, and starting morphology PZT powders. The final dielectric properties of the device depend markedly on PZT grain size, second phase content, purity, stoichiometry, and controlled by the processing condition[9].

In addition, Ferroelectric(PZT) ceramics which was prepared by the sol-gel exhibited excellent homogeneity. The condensation of metals alkoxide and hydrolysis with different modifiers included acetic acid, acetylacetone, and 2-methoxylethanol[10]. “The Advantage of this new method is the capability of producing controlled nano-scale PZT ceramics powder with specific crystalline phase”[11]. Metal oxides with a general stoichiometric formula of ABX₃ may form a perovskite structure. In one variation, the “A” cation is more abundant, and where “B” is a metal ion and “X” is a halogen (O, I, etc...)[12]. Metal oxide prepared by sol-gel techniques that used complicated procedures should be content many refluxing steps[13].

For PZT compound is a solid-solution phase that has chemical formula Pb(ZrₓTi₁₋ₓ)O₃. According to the ABO₃, A, B cation occupies a different place in the unit cell. The B cation occupies the center of the unit cell and has the charge more massive than the A cation. In PZT compounds Zr, Ti is representing B cation, and oxygen atoms are surrounding the cell are enlisted to balance the charge of perovskite materials with its nature cubic shape. Oxygen and lead ions have radii about 1.4 nm to make up face center cubic array, which has a lattice parameter 0.4 nm as shown in Figure (1)[14].

“A morphotropic phase boundary consists of two regions of the ferroelectric phase. The tetragonal phase appeared on part Ti-rich, and another region has a rhombohedral phase with Zr-rich. At room temperature, this boundary is at the point Zr/Ti = 52/48”[15].
The Curie temperature is represented maximum dielectric constant value through the process of seeing the variation of dielectric constant as function temperature with a range of frequencies[16]. The objective of the present paper is to investigate the influence of sintering temperature conditions for PZT ceramics which is prepared by the sol-gel method. The sintering temperature influenced electrical properties and nanostructure because it affected particle size with different sintering temperatures.

2. Experimental details

The synthesis of Lead Zirconium Titanate powders carried out that used the precursor solution of Pb(Zr0.35Ti0.65)O3 (PZT) was prepared by the Sol-Gel Method. Precursors prepared using Lead Acetate Trihydrate((Pb(CH3COO)2.3H2O) 99.99%, Sigma-Aldrich) Zirconium propoxide((Zr(OCH2CH2CH3)4, 70% a Sigma-Aldrich) and Titanium(IV) isopropoxide ((Ti(OCH(CH3)2)4, 97% Sigma-Aldrich) as starting materials. First, the synthesis began with dissolving 0.4 M of Lead acetate in acetic acid and the solution put on a magnetic stirrer (40 °C, 30 min), the second stage, Zirconium propoxide dissolved in isopropanol and also stirrer (40 °C, 30 min) and mixed into the lead acetate precursors solution. After dissolving lead acetate and Zirconium propoxide then the solution refluxed 2 h at 110 °C till getting the transparent solution. The solvent 2-methoxy ethanol was added to titanium isopropoxide for stabilizer structure at room temperature, the solution, and was stirred by magnetic stirrer at R.T until it was turned into thick white gel. The mixture was adjusted to have the value of PH4.5-5. The total solution was refluxed by refluxed system tow hours at 110 °C to get thick yellow-white good homogenous for the solution.

The colloidal solution was cooled to room temperature and then was dried by a furnace at 120 °C to remove water. The thick gel was put in the furnace at 200 °C (3 h) to get white-yellow powders. These powders were grounded by pastel and mortar till getting fine powders. After that, the compact was prepared by pressing in a hydraulic press at pressure 250 Pa. Later on, they were calcined at 600 °C for three h to complete the crystallization of ferroelectric PZT ceramics. The powders were sintered as form disk shape compact of diameter 1.2 cm and high 2.5 mm. Conventional ceramics sintering was carried out in furnace has a high degree in an air atmosphere for three h. A procedure of fabrication of the ceramic sample was repeated once again, so every batch of pellets sintered three times.

The pellets were sintered at different temperatures (850, 1050, 1150 °C) to overcome cracks and vacancies in PZT samples, responsible for this action is due to the increase in density with increasing temperature.
Field emission scanning electron spectroscopy’ (FESEM) (Hitachi 4700) used to study the morphology surface of the sintering pellets and composition by energy dispersive spectroscopy. Discovery and identification of phases were performed at R.T by using XRD powder diffractometer with CuKα (λ=1.5418 Å, 30 kV, 30 mA) model (Bruker, Germany) in a wide range of (2θ= 20-80) at scanning rate two min-1. Dielectric measurement using an LCR meter device in the experimental details, An LCR meter is a type of electronic test equipment used to measure the inductance (L), capacitance (C), and resistance (R) of an electronic component

3. Results & discussion

Micrograph by scanning electronic spectroscopy of surface morphologies the Pb(Zr 0.35Ti0.65)O3 powders were sintered at (850, 1050, 1150 °C) 3 h shown in the figure. (2). It was observed that the temperature of sintering affected grain size. The average particle size of PZT powder was determined by means SEM or XRD using the Scherrer equation. It was observed that the average particle size increasing as the temperature of sintering increased.

The temperature of sintering has increased the small particles and tended to merge to become larger ones. The starting concentration and reaction time (reflux time &stirrer time) parameters of synthesis have a significant influence on the nanostructure size of Pb0.35Zr0.65TiO3.

It should also be noted that temperatures from 400 to 600 were calcined temperature to complete the crystallinity phase for PZT compounds, these were not sintered temperatures. By controlling these parameters, the particle size change to be (92.65,33, 132.54, 165.87 nm) corresponding to temperatures rise (850, 1050, 1150 °C), respectively. The temperature of sintering was increased, which was led to an increase in the particle size of PZT due to reducing porosity with increased density. Some previous papers agree with the results of [5,16,17]

Figure 2. Images of Field emission scanning electron spectroscopy (FESEM) for Pb(Zr0.35Ti0.65)O3 (a) 400 °C (b) 500 °C (c) 600 °C (d) 850 °C (e) 1050 °C (f) 1150 °C.
XRD patterns of Pb(Zr0.35Ti0.65)O3 shown in the figure. (3), it has been seen compound sintering at (850, 1050, 1150 C) were polycrystalline phases with perovskite structure. Also, intermediate phases shown in XRD patterns. In the unit cell, the Zr or Ti cationion was replaced with maintaining the perovskite structure. Figure (3), Many peaks were shown by XRD pattern correspond to (100), (101), (111), [(200),(002)],[(201),(210)], [(211),(112)] and [(220),(202)], planes. These peaks are related to the tetragonal PZT phase, and the peaks perfectly match with pdf card (JCPDS file No. 33-784), the lattice constant a=4.0267146 Å, c=4.140146 Å with Pm3m space group[5]. The results of the PZT compound calcined up at 400 °C comprised the amorphous structure. Crystallinity degree was increased with increasing temperature of calcination, and perovskite types structure form appeared. The complete crystalline PZT powders were achieved at a temperature above 600-700 °C and its peaks corresponding to the tetragonal structure. Figure (3) shows tiny of unknown phase also exists at (29°) is believed to be caused by an inhomogeneous distribution of elements component in the sol. Some researchers have referred to this unknown phase as a pyrochlore phase. The samples calcination above 600 were exhibited with a free pyrochlore phase. The amount of pyrochlore phase was decreased at temperature 400 to 700 °C and increasing the perovskite phase gradually. Above 600 °C, the sharpness of the tetragonal perovskite was increased with increasing temperature. The PZT powder was sintered at different temperatures found to the preparation of green pellets, the powders the density variation of the PZT ceramics as a function of sintering temperature. The samples were sintered at 1150°C for (3 h) have a relative density of 90.5 %.

![Figure 3. XRD patterns of Pd(Zr0.35Ti0.65)O3 powders with various sintering temperatures.](image)

Furthermore, it has been found by SEM images the grain distribution of PZT ceramics which was sintered at 1150 °C is the most uniform. The sintering temperature increased the Intensity of peaks was increased. It has been explained that the crystalline complete and disappeared intermediate phases due to the effect of sintering temperature.
The increase in the sintering temperature leads to an increase in the particle size, which in turn leads to a decrease in the interatomic space. The decrease in interatomic space leads a shift to a higher angle with increased sintering temperature.

For the dielectric measurements, the PZT discs were lapped 1.2 cm diameter and 2.5mm thick, cleaned, and sintering at different sintering temperatures. The thermal evaporation used to fabricate Au electrodes on both sides of pellets. The dielectric calculated from LCR mater which was obtained at room temperature using single 0.1 V, in a frequencies range (1 kHz, 50 kHz, and 100 kHz). The rising of sintering temperature leads to an increase in the dielectric constant that belongs to better crystallinity and increased gain size. It has been observed that any phase-type the dielectric properties will be closed relation to the lattice parameters with regard tetragonal phase the value of dielectric increased with increasing distortion of lattice relative to the cubic symmetry decreases.

The crystallinity, grain size, and porosity was affected the value of dielectric constant, which has been carried out at different temperatures (850, 1050, 1150 °C). The dielectric constant has been reduced at a lower temperature that attributes to smaller grain size and poor crystallinity.

Dielectric properties depend on frequencies at various sintering temperatures to Pb(Zr0.35Ti0.65)O3 ceramics. Figure (4) illustrates the dielectric constant of Pb(Zr0.35Ti0.65)O3 sintering at (850, 1050, 1150 °C) decreases as the frequency increases. The behavior is attributed to different types of polarisation mechanisms; the dielectric constant decreases due to dipole polarization and space charge cannot catch up with relaxation time of ferroelectric materials as frequency increased. The dielectric loss of Pb(Zr0.35Ti0.65)O3sintering at (850, 1050,1100 °C ) decreases continuously with frequency increases, as shown in figure (5). It is clear from figures (4), the values of the dielectric constant increases from 635 to 1165 due to the increased sintering temperature.

Figure (6 ) shows the dielectric constant vs. temperature with a range of frequencies (1, 50, 100 kHz), the constant dielectric increases initial till it reaches the curie temperature of PZT ceramics, at room temperature,390 °C’ which sintering at (850,1050,1150 °C) and no significate change with increased sintering temperature.
Figure (4) Dielectric constant as function frequency with (a-850, b-1050, c-1150 °C)
Figure (5) Dielectric loss as function frequency with (a-850, b-1050, c-1150 °C)
Figure (6) Dielectric constant as function temperature with (a-850, b-1050, c-1150 °C)
4. Conclusions

Ferroelectric Lead Zirconate Titanate (PZT) compound was prepared by the sol-gel method. Acetic acid used as a solvent to zirconium propoxide and acetate of lead. Ethoxy methanol was utilized as a stabilizer for titanate(IV) isopropoxide. The sintering temperature affected significantly dielectric properties and the microstructure of the PZT compound. Pure PZT nanoparticles were synthesized by a modified sol-gel process and characterized by powder XRD, SEM. A conventional ceramic procedure was prepared the parameters of the crystalline structure of the samples, sintering at different sintering temperature change with the composition that which turn on physical and chemical properties such as dielectric properties, and these changes are more pronounced inside the coexistence phase region.

Morphology surface of PZT ceramics exhibited various particles size ranging from (92.65,33, 132.54, 165.87 nm) depend on the degree sintering temperature (850, 1050, 1150 °C) was detected by SEM. The particle size increased with increasing sintering temperature.

XRD pattern of Pb(Zr0.35Ti0.65)O3 shows a tetragonal phase with constant lattice a=3.965 A and Pm3m space group. A small amount of phase was found to exist along with the perovskite phase. Grain size increased due to increase sintering temperature, which in turn decreased interatomic space. Dielectric properties ($\varepsilon$, $\delta$) increased with rising sintering temperature. The increasing frequency leads to a decrease in the dielectric constant and dielectric loss at different temperatures.

The value of the dielectric constant appeared to be significantly affected by the type of phase that belongs due to the distortions in the constant lattice relative to the cubic phase.

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