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Synthesis and characterization of lead titanate nanopowders by organic acid precursor

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Lead titanate $PbTiO_3$ nanopowders have been synthesized using organic acid precursors method. Effects of synthesis conditions namely, annealing temperature (500-1000 ^{0}C), annealing time (1-2 h) and type of organic acid (oxalic, tartaric, and citric acids) on the phase formation, morphology and dielectric properties were studied. The produced lead titanate powders were investigated using X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM) and impedance analyzer. The results obtained showed that pure single tetragonal $PbTiO_3$ phase was obtained for thermally treated precursors at 600^{0}C with annealing time 1, 1.5 and 2 h using oxalic, tartaric and citric acids, respectively. The crystallite size of the pure $PbTiO_3$ was in the range between 28.3 to 32 nm. SEM and TEM micrographs showed that the organic acid types have significant change in the morphology of the produced lead titanate powder. The dielectric properties were increased using organic precursor method compared by the powders obtained by other methods. The high dielectric constant values are excellent for using in embedded capacitor applications.

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Keywords: Lead titanate, Synthesis, Characterization, Nanopowders, Dielectric constant

1. Introduction

Lead titanate, $PbTiO_3$, is one of the simplest and the most important members ferroelectric, pyroelectric and piezoelectric materials with perovskite structure ABO_3 where A is a monovalent or divalent cation with large radius, B is pentavalent or tetravalent cation with small radius and O is oxygen (1). Owing to their ferroelectric nature, $PbTiO_3$ show high spontaneous polarization (75-88 $\mu C/cm^2$), high dielectric constant and high Curie temperature of 490 ^{o}C. At this temperature, the material undergoes a first order transition from high temperature paraelectric phase with higher symmetry and then without spontaneous (Pm3m cubic perovskite structure) into a low temperature ferroelectric phase (P4 mm tetragonal perovskite structure). At room temperature, it exhibits a lattice parameter of c= 4.150 Å and a= 3.904 Å, thus giving a c/a as high as 1.063 (2). This material is suited and widely used in capacitors applications as energy storage, current blocking, electrical noise filtering and high frequency tunning devices. Furthermore, $PbTiO_3$ mostly displays positive temperature coefficient (PTC), making it useful materials for thermistors and self-regulating electric heating systems. In addition, $PbTiO_3$ is mostly used in dynamic random access memories (DRAM), non-volatile memories and positive temperature coefficient resistors (PTCR). Moreover, according to piezoelectric properties of $PbTiO_3$, this material is considered as smart material and it can employed as sensors and actuators, sound and ultrasound transducer and electrooptic devices (3-9). Also, Owing to their pyroelectric characterization, $PbTiO_3$ is used as Infrared detector for military night vision, target acquisition and missile guidance. Non military applications include infrared detection head in imaging system for product inspection in faults isolation assuring quality, automotive vision, fire detection and medical diagnostics (10).

Many groups in the literature have synthesized lead titanate by solid state reaction (11-12) and wet chemical methods. The wet methods are including sol gel (13-15), co-precipitation (16), microemulsion (17), hydrothermal (18-19) and organic acid precursor methods (20-21). The organic carboxylic acid precursor technique involves the preparation of aqueous solution required cations, the chelation of cations in solution by addition of carboxylic acid. Then, the temperature of the solution is raised to give polymeric viscous precursors. The precursors are calcined at low temperature compared with other method. The carboxylic acid was not only used to form stable complex with starting metallic ions but also it used as organic rich fuel. The process is very simple and available for most piezoelectric materials. Moreover, the advantages of organic acid precursor process are the low cost starting materials, fine microstructure, high performance, homogeneity, narrow particle size distribution and friendly environment (21-23). This method is also called combustion method, polymeric precursor acid, acids gel method (oxalic acid, tartaric acid, lactic acid, etc) and also Pechini-type process (citrate precursor method).

From our knowledge, no data mentioned in literature about the synthesis of lead titanate nanopowders via organic acid precursors using titanium dioxide as a source of titanium. In addition, the effect of type of organic acid on the phase formation, microstructure and dielectric constant of lead titanate powders is not mentioned before. In this work, we reported about the synthesis of lead titanate nanopowders using organic acid precursor method using lead acetate and titanium dioxide using different

type of organic acids (oxalic, tartaric and citric acids). Moreover, Effects of synthesis conditions on the phase formation, crystalline size, microstructure and dielectric constant were systematically studied.

2. Experimental

$PbTiO_3$ nanopowders were prepared using organic acid precursor method using pure chemical grade lead acetate $(CH_3COO)_2Pb$ 99% purity and titanium dioxide TiO_2 99.8 % purity in the presence of stoichiometric amount of organic acid (oxalic, citric, and tartaric acids 99.5% purity). The molar ratios of Pb^{2+}: Ti^{4+} ions were stable at 1. The molar ratios of the organic acids were added according to the reaction of 1 mole of the acid with both Pb^{2+} and Ti^{4+} ions according to the following equations using oxalic acid as example:

$$Pb^{2+} + C_2O_4^{2-} \rightarrow PbC_2O_4 \quad (1)$$

$$TiO_2 + H_2C_2O_4 \rightarrow TiOC_2O_4 + H_2O \quad (2)$$

$$PbC_2O_4 + TiOC_2O_4 \rightarrow PbO + TiO_2^* + 2CO + 2CO_2 \quad (3)$$

$$PbO + TiO_2^* \rightarrow PbTiO_3 + CO_2 \quad (4)$$

The solution was stirred and gently evaporated at 80 ^{o}C till a clear, viscous resin was obtained, then dried at 110 ^{o}C for 24 h. The dry precursors were heated (calcined) at a rate of 10 ^{o}C / min in static air atmosphere up to required different temperatures from 500 to 1000 ^{o}C at different calcined times from 1-2 h. The final products were characterized using X-ray diffraction (XRD) on a Bruker axis D8 diffractometer using Cu Kα radiation (λ=1.504 Å). The average crystallite size of the powders was estimated automatically from corresponding XRD data using X-ray line-broadening technique employing the classical Debye-Scherrer formula for the most intense peak (101) plane determined from the X-ray diffraction data according to the following equation:

$$d_{RX} = k\lambda/\beta \cos\theta \quad (5)$$

Where d_{RX} is the crystallite size, k = 0.9 is a correction factor to account for particle shapes, β is the full width at half maximum (FWHM) of the most intense diffraction peak (101) plane, λ is the wavelength of Cu target = 1.5406 Å, and θ is the Bragg angle. The micrographs of $PbTiO_3$ samples were examined by direct observation via scanning electron microscopy (JEOL, JSM-5400). The transmission electron microscope (TEM, JEOL -1230) operating at 80 KV was used to confirm the crystallographic setting and to study the microstructure of the lead titanate powders. The dielectric properties of the produced lead titanate samples were carried out using the impedance analyzer HIOKI 3532-50 LCR HiTester; Japan with frequency ranges from 42 Hz to 5 MHz.

3. Results and discussion

X-ray diffraction patterns of the formed lead titanate powders for thermally treated precursors at different temperatures from 500 to 1000 ^{o}C, calcination time 2 h using different organic acids (oxalic, citric and tartaric acids) were given in Fig. 1. A pure well crystalline tetragonal $PbTiO_3$ phase (JCPDS # 75-438) was formed at calcination temperature 600^{o}C and calcination time 2 h using different organic acids. The crystallinity of the produced phase was increased with the increasing calcination temperature from 600 to 1000 ^{o}C. The diffraction peaks corresponding to diffraction planes (101), (110), (100), (001), (200) and (211) which ascribed to tetragonal $PbTiO_3$ phase were obtained. On the other hand, the decreasing of the calcination temperature to 500 ^{o}C led to form of the mixture of leads titanate $PbTiO_3$, lead oxide PbO and titanium dioxide TiO_2 phases.

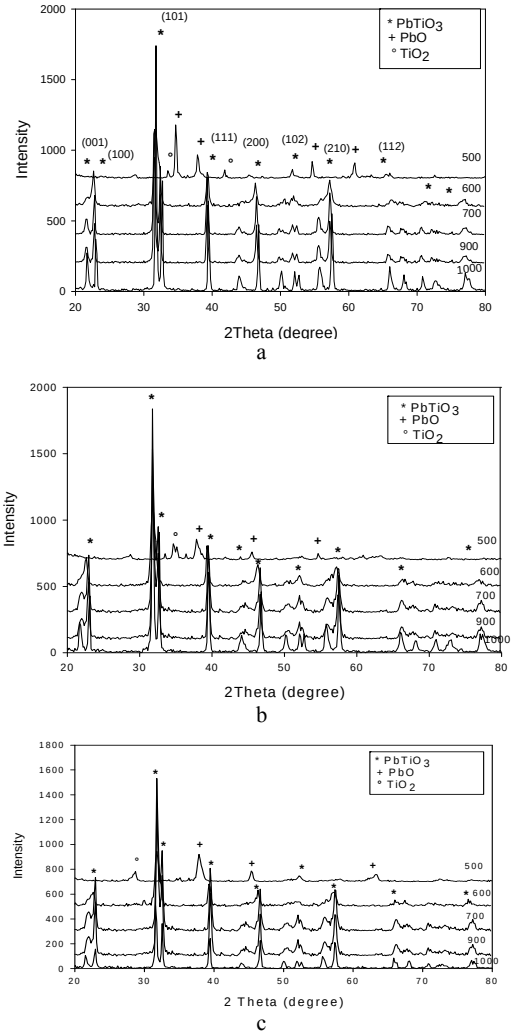


Fig. 1. XRD patterns of lead titanate nanopowders synthesized by organic acid precursor at different calcination temperatures from 500 to 1000 ^{o}C and calcination time 2h using (a) oxalic acid (b) tartaric acid (c) citric acid.

The conversion, % of the $PbTiO_3$ phase at different calcination temperatures (500-1000 °C), calcination time 2 h using oxalic, tartaric and citric acids were listed in Table 1. The conversion, % of the precursors to lead titanate phase was estimated qualitatively from XRD results using the following relation:

$$\% \text{ conversion} = \frac{I_1}{I_1 + I_2 + I_3} \times 100 \quad (6)$$

Where: I_1, I_2 and I_3 are the intensities of the main peaks of various phases.

From Table 1, the results showed that the lead titanate conversion, % was 80, 53.3 and 81.1% at 500 °C for oxalic, tartaric and citric acids, respectively. Increasing the calcination temperature up to 600-1000 °C led to form of the 100% conversion of tetragonal $PbTiO_3$ phase. This finding was observed in all types of organic acids (oxalic, tartaric and citric acids). The crystallite size of the produced tetragonal $PbTiO_3$ phase was increased by increasing the temperature. It increased from 32.0 to 103.5 nm when the calcination temperature increased from 600 to 1000 °C for oxalic acid precursor. Moreover, the crystallite size of lead titanate increased from 28.3 to 90.9 nm when the calcination temperature increased from 600 to 1000 °C using tartaric acid as organic acid precursor. On the other hand, the crystallite size of lead titanate was increased from 32.6 to 91.4 nm for citrate precursor.

Table 1. The phase conversion, % and the crystallite size of the lead titanate phase nanopowders at different calcination temperature from 500 to 1000 °C and calcination time 2 h for oxalic, tartaric and citric acids.

Precursor	Temperature, °C									
	500		600		700		900		1000	
	* C, %	**Cs, nm	C, %	Cs, nm	C, %	Cs, nm	C, %	Cs, nm	C, %	Cs, nm
Oxalic acid	80	-	100	32.0	100	34.4	100	85.5	100	103.5
Tartaric acid	53.3	-	100	28.3	100	32.0	100	55.0	100	90.9
Citric acid	81.1	-	100	32.6	100	33.6	100	59.6	100	92.4

* C means phase conversion, %
**Cs means crystallite size, nm

To study the effect of calcination time on the lead titanate phase formation, a series of experiments was carried out at molar ratios 1 of the carboxylic acids and calcination temperature 600 °C at different calcination time from 1-2 h. Fig. 2 Shows XRD patterns of the produced powders using the three different carboxylic acids at different calcination time and calcination temperature 600 °C. From the results, at calcination time 1h using oxalic acid as a source of carboxylic acid (Fig. 2a), the formed tetragonal $PbTiO_3$ phase contained some impurity peaks, which were related to lead oxide PbO and titanium dioxide TiO_2 phases. At calcination time 1.5 and 2h, a well-crystallized pure single tetragonal $PbTiO_3$ phase was formed. The average crystallite size of the formed lead titanate observed for the precursor annealed at 600 °C for 1.5 h was around 29.4 nm. By using tartaric (Fig. 2b) and citric acids (Fig. 3c) as a source of carboxylic acids, a formation of pure single phase of lead titanate was only obtained at calcination time 2 h with a crystallite sizes of 28.3 and 32.6 nm for tartaric and citric acids, respectively. At lower annealing time than 2h, the formed tetragonal $PbTiO_3$ phase contained some impurity peaks, which are related to lead oxide PbO phase.

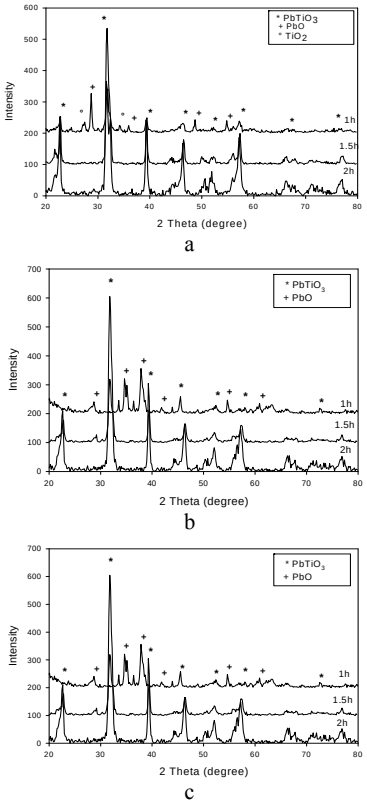


Fig. 2. XRD patterns of lead titanate nanopowders at different calcination times 1-2 h for calcination temperature 600 °C using (a) oxalic acid (b) tartaric acid (c) citric acid.

It is the worth to mention that organic acid precursor method is a successful and low cost method for preparation of lead titanate nanopowders since in our study; it depends on the commercial chemical such as titanium dioxide, lead acetate, oxalic, tartaric and citric acids which are available. In similar studies, several authors have been obtained the tetragonal lead titanate phase by the same method using expensive starting materials. Paris et al. [22] used citric acid as organic carboxylic acid for synthesis of lead titanate while they used lead acetate and titanium iso-propoxide as the source of lead and titanium, respectively, in the presence of ethylene glycol. They conclude that the formation lead titanate was obtained at 600 °C for 2 h .Pontes et al [23] applied the similar method of Paris et al. The difference was the heating of the solution at 80-90 until become more viscous then dried at 150 °C for 20 min, and then heating the mixture at 350 °C for 2h to form precursor. Lead titanate phase formed after calcination temperature 500 °C for 4 h.

SEM images of the lead titanate powders produced by organic acid precursor method using different types of carboxylic acids (oxalic, tartaric and citric acids) were given in Fig. 3 for the powder annealed at 1000 °C for 2 h. The images showed that the formed lead titanate (PT) particles were homogenous and the grain size was very fine for lead titanate nanopowders produced by tartaric acid precursor compared with oxalic and citric acids. Moreover, most of particles were presented in tetragonal-like structure.

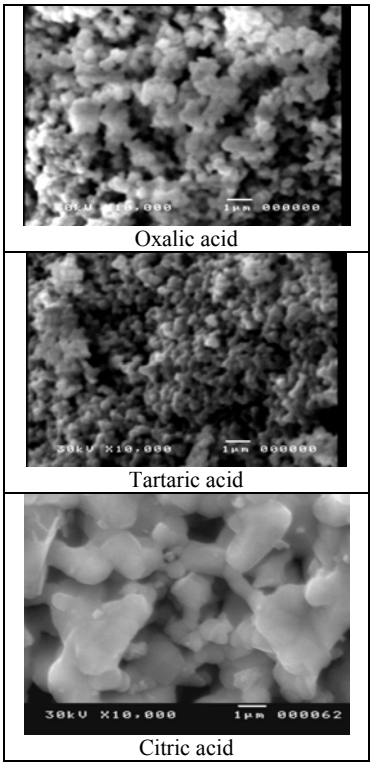


Fig. 3. SEM micrographs of the produced lead titanate nanopowders at calcination temperature 1000 °C and calcination time 2h for different organic acid precursors.

Fig. 4 showed the TEM micrographs of tetragonal lead titanate $PbTiO_3$ powders produced at calcination temperature 600 °C and calcination time 2h using oxalic, tartaric and citric acids as organic precursors. As shown, the produced $PbTiO_3$ nanospheres with a uniform morphologies and narrow size distribution were obtained. The particle size of the produced powders was 37, 15 and 47 nm for oxalic, tartaric and citric acid, respectively. The decreasing in grain size with tartaric acid explained the increasing in dielectric constant at low frequencies when compared with other carboxylic acids.

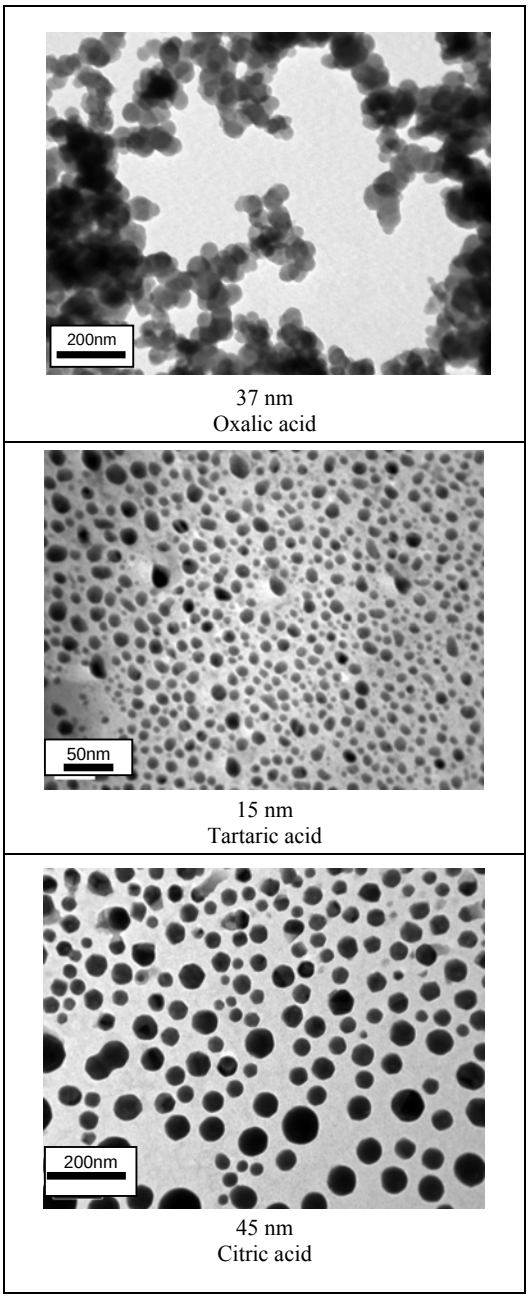
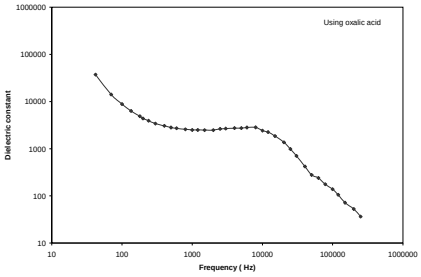
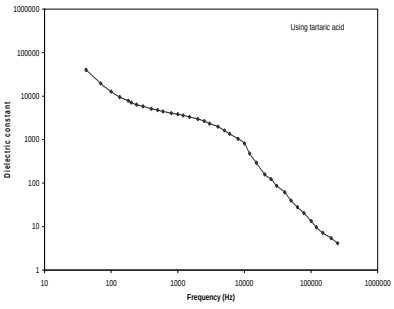


Fig. 4. TEM images of the produced lead titanate nanopowders at calcination temperature 600 °C and calcination time 2 h using different organic acid precursors.

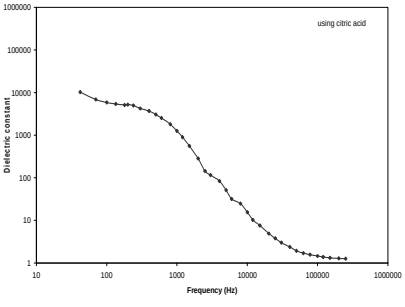
Fig. 5 showed the dielectric constant of produced lead titanate powders at calcination temperature 600 °C, calcination time 2h using oxalic, tartaric and citric acids which were determined by impedance analyzer at room temperature. It can be observed that, for an each experiment, the values of dielectric constant decreased with increased the frequency due to a decrease in the dipolar polarization of the matrix and the accumulation of charges at the interface between particles. The obtained dielectric constant of lead titanate using oxalic acid as source of carboxylic acid at room temperature was 8801and 2506 at 100Hz and 1 kHz, respectively. Then, the value was found to fall rapidly with increasing frequency. The dielectric constant of lead titanate prepared by using tartaric acid at room temperature was 12702 and 3840 while the dielectric constant of lead titanate prepared by using citric acid at room temperature was 5836 and 1255 at 100 Hz and 1 kHz, respectively. The increasing in the dielectric constant value at low frequency with tartaric acid was attributed to the decreasing in the particle size compared with oxalic and citric acids.



a



b



c

Fig. 5. Dielectric constant of lead titanate powders at calcination temperature 600 °C and calcination time 2 h using (a) oxalic acid (b) tartaric acid (c) citric acid.

4. Conclusion

Tetragonal lead titanate $PbTiO_3$ nanopowders (28.3-103.5 nm) have been synthesized using organic acid precursor method. Effects of calcination temperature, calcination time and organic acids types (oxalic, tartaric and citric acids) on the crystal structure, crystalline size, microstructure and dielectric constant of the produced $PbTiO_3$ nanopowders have been studied in details. A well crystalline single phase of tetragonal lead titanate powders was obtained at different organic acids (oxalic, tartaric and citric acids) at different calcination temperatures from 600 to 1000 °C and calcination time 2h.

The smallest crystallite size in the range 28- 32 nm can be obtained crystalline size at low calcination temperature 600 °C and calcination time 2h using oxalic, tartaric and citric acids. In contrast, the crystallite size 91-103.5 nm using different carboxylic acids can be obtained at increasing temperature up to 1000 °C. TEM micrographs showed that the produced pure PT nanopowders were formed in the nanospheres with narrow particle size distribution. Dielectric constant of lead titanate powders using oxalic, tartaric and citric was increased by decreasing the frequency and the value was increased using tartaric acid compared with oxalic and citric acids as organic precursors.

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