

RESEARCH ARTICLE

Influence of heat treatment on synthesis of stoichiometric perovskite PbTiO_3 nanostructure via hydrothermal method

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ABSTRACT

In this research, the stoichiometric perovskite lead titanate (PbTiO_3) nanostructure was synthesized successfully by the hydrothermal method. The effect of heat treatment of the autoclave and the furnace on the structure of this material was investigated. Titanium dioxide (TiO_2), titanium tetrachloride (TiCl_4) and lead oxide (PbO), lead nitrate ($\text{Pb}(\text{NO}_3)_2$) were used as the titanium and lead sources, respectively. The negative amount of the Gibbs free energy shows the reactivity of the reaction at room temperature. Characterization of PbTiO_3 was carried out using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). The amount of lead titanate increased by raising the temperature of the autoclave. The objective of this research was developing the hydrothermal method to produce the phase-pure lead titanate at lower temperatures; also the effect of the precursor materials and heat treatment on morphology and crystal grows the development of PbTiO_3 nanopowders were investigated. There are not any secondary phases when the sample was calcined at high temperatures. It seemed that heating in the furnace in a longer period and higher temperatures could affect the size of the crystallites. The powder was heated at 1200 °C had the larger grains and the ferroelectric domains that may cause the lowering of the dielectric constant.

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INTRODUCTION

The perovskites structure is a group of ceramic with the general formula ABX_3 (A and B are two cations with different sizes ($A > B$), X is an anion that binds with both cations) which discovered by Gustav Ros in 1839 [1,2]. More than 20 elements have been known to occupy the A-site position, and more than 50 elements have been found to occupy the B-site in perovskites [3].

Lead titanate (PbTiO_3) exhibits a perovskite structure and a Curie temperature of 490 °C [4]. It is widely used in optoelectronics, transducers, sensors, resonators, transducers, and non-volatile memory components due to its remarkable ferroelectric, pyroelectric, piezoelectric and low dielectric constant properties [5-7].

A very interesting application of this material

is because of its high spontaneous polarization to paraelectric at 763 K which is the highest amount between the perovskites group [8]. PbTiO_3 has a tetragonal phase with a c/a ratio of 1.063 at room temperature and a cubic structure above 763 K [9], and the wide temperature stability of the ferroelectric phase (the transition of ferroelectric). Recently, the powders in nano-sized scales are considered to be suitable in different industries, especially in electronics, biomaterials, pharmacology, etc. The finer ceramic powders improve the electronic properties of the devices. The PbTiO_3 nanostructures are very attractive due to they are promising candidates for high-density, non-volatile information storage and scanning probe-based ferroelectric mass storage [5]. The formation of PbTiO_3 ranging from nanometer to micrometer sizes helps the sintering of this material

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Table 1: The hydrothermal condition for synthesis of PbTiO₃.

Sample	Precursors	Autoclave condition (temperature (°C), time (h))	Furnace condition (temperature (°C), time (h))
1	Pb(NO ₃) ₂ , TiCl ₄	180, 2 (in ethanol)	-
2	Pb(NO ₃) ₂ , TiCl ₄	220, 2 (in ethanol)	-
3	Pb(NO ₃) ₂ , TiCl ₄	240, 2 (in ethanol)	-
4	Pb(NO ₃) ₂ , TiCl ₄	220, 2 (in ethanol)	500, 1
5	Pb(NO ₃) ₂ , TiCl ₄	240, 2 (in water)	500, 1
6	Pb(NO ₃) ₂ , TiCl ₄	240, 6 (in ethanol)	900, 6
7	PbO, TiCl ₄	240, 6 (in ethanol)	900, 6
8	Pb(NO ₃) ₂ , TiO ₂	240, 6 (in ethanol)	900, 6
9	Pb(NO ₃) ₂ , TiCl ₄	240, 6 (in ethanol)	1200, 8
10	Pb(NO ₃) ₂ , TiCl ₄	240, 2 (in water)	1200, 8
11	Pb(NO ₃) ₂ , TiCl ₄	180, 2 (in ethanol)	1200, 8

and decrease the temperature of the ferroelectric phase.

The conventional solid-state methods are usually possible at temperatures at which loss of volatile lead becomes a problem [9]. Achieving to nanostructure PbTiO₃ with a homogeneous structure cannot be obtained by solid-state methods [10]. Among different chemical techniques for synthesis of PbTiO₃, e.g. sol-gel [11], co-precipitation [12,13] emulsion [14] polymerized complex [15]. Hydrothermal method has been used for the synthesis of many kinds of nanomaterials [16-18]. This technique is one of the most suitable chemical methods in terms of energy consumption and environmental friendliness for the preparation of a vast number of perovskite compounds with specific crystalline structures and chemical compositions [19].

The hydrothermal reaction has a particular advantage of low reaction temperature, less than 200 °C which is below the Curie temperature [20,21]. The controllability on phase formation, chemical stoichiometry, particle size and morphology by simply fine-tuning the processing parameters is possible by this method [22]. Hydrothermal formation of lead titanate has been broadly studied. In order to control the morphology of powders during the hydrothermal process several items such as temperature, precursors and pH has to be optimized. Cho et al. [23] were used the thermodynamic modeling to predict the optimum synthesis conditions for precipitation of the phase-pure lead titanate. Wang et al. prepared PbTiO₃ nanorods by phase transformation from Pb₂Ti₂O₆ nanorods [24]. Chankaew et al. used the ultrasonication and hydrothermal process

for the synthesis of lead titanate at water boiling temperature [20]. The nano-sized powder of lead titanate has been synthesized via a hydrothermal process with inexpensive precursors by Deng and his colleagues [25].

In this research, the nanostructure lead titanate synthesized by the hydrothermal method at low temperature. The effect of heat treatment of the autoclave and the furnace on the structure of this material was investigated. The objective of this research is to develop a hydrothermal synthesis method to produce phase-pure lead titanate at lower temperatures; also the effect of precursor materials and heat treatment on morphology and crystal grows the development of PbTiO₃ nanopowders.

EXPERIMENTAL PROCEDURES

In order to the synthesis of PbTiO₃ by hydrothermal method, titanium dioxide (TiO₂), titanium tetrachloride (TiCl₄), lead oxide (PbO), lead nitrate (Pb(NO₃)₂), potassium hydroxide (KOH), ethanol and distilled water were used. All the chemicals were of analytical grade purity. First, appropriate amounts of lead nitrate or lead oxide were dissolved in ethanol. The proper amount of titanium tetrachloride or titanium dioxide was dissolved in ethanol. Subsequently, the lead solutions were dropped into the nitrate solutions under constant magnetic stirring. The precursors and conditions are different for each sample (Table 1). The pH was adjusted by adding KOH in the solution. The specimens were heated in an autoclave in special temperatures and times and then cooled to room temperature naturally (Table 1). The obtained products were filtered, washed with distilled water and absolute ethanol several

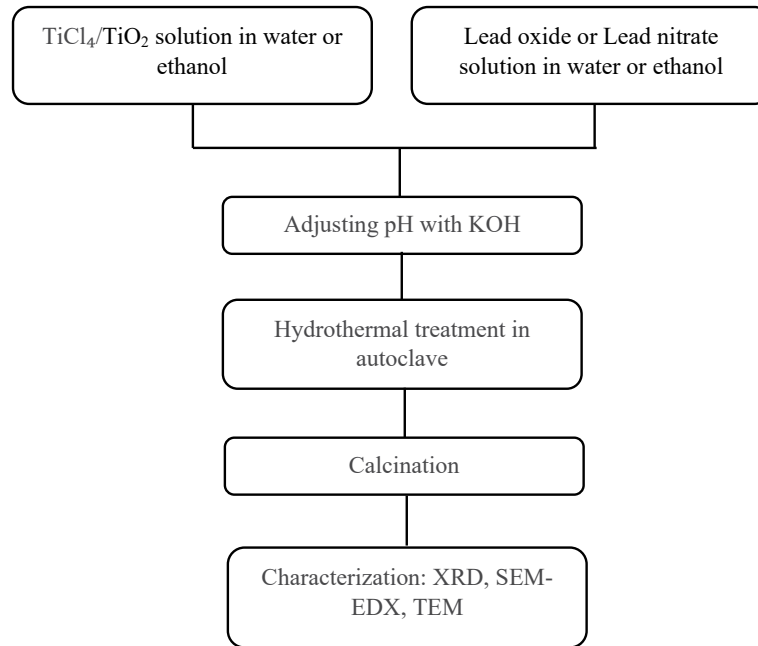


Fig. 1. Schematic diagram of the hydrothermal synthesis of PbTiO₃.

times, and dried at 70 °C for 4 h. The final powders were straightly used for characterization.

X-ray diffraction (XRD, Philips TW1800, CuK_α, λ=1.54178 Å), was used to characterize the crystalline phases of the samples. Scanning electron microscope (SEM, Tescan Vega II XMU) equipped with an energy dispersive X-ray (EDX) analysis was employed for observation of particle morphology, size, and elemental composition. TEM and images were obtained using a transmission electron microscope (TEM). The schematic of the hydrothermal process for the synthesis of PbTiO₃ is shown in Fig. 1.

X-ray diffraction is a proper method for determining the mean size of nanocrystallites in nano-sized materials. The size of the crystallites was estimated by the Scherrer equation [26]:

$$D = \frac{K\lambda}{B_1 \cos\theta} \quad (1)$$

th D, the size of the crystallite in Å, K, the shape factor of the average crystallite (approximately equals 0.9), λ, the wavelength of the X-ray i.e. 1.54056 Å, θ, the Bragg angle of the diffracted peak and $\frac{B_1}{2}$ the parameter calculated in radians as the below:

$$B_{1/2} = (B_m^2 - B_s^2)^{\frac{1}{2}} \quad (2)$$

here B_m, is the peak width at half-maximum of the sample and B_s is the peak width at half-maximum of the standard sample.

RESULTS AND DISCUSSION

Lead titanate is a very interesting material because of its high spontaneous polarization to paraelectric at 763 K. It is one of the most important ferroelectric materials. It is discussed in the introduction about the benefits of the hydrothermal method for the synthesis of PbTiO₃.

In order to find the thermodynamic possibility for the formation mechanism of the lead titanate, the Gibbs energy (ΔG°) of formation has to be calculated. The change in the Gibbs free energy of the system that occurs during a reaction is therefore equal to the change in the enthalpy (ΔH°) of the system minus the change in the product of the temperature times the entropy (ΔS°) of the system.

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (3)$$



The amounts of enthalpy and entropy of the precursors and the calcium titanate are written

Table 2: The amounts of enthalpy and entropy of the precursors and lead titanate [18].

Materials	ΔS°_{298} (J/molK)	$-\Delta H^{\circ}_{298}$ (kJ/mol)
PbO	68.70	217.3
TiO ₂	49.9	939.7
PbTiO ₃	5.8–7.3	36.7

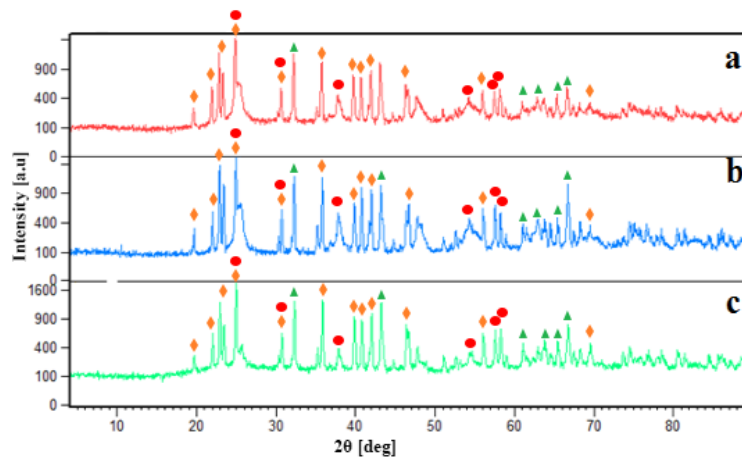


Fig. 2. XRD of the samples was maintained in an autoclave at; a) 180 °C, b) 220 °C and c) 240 °C for 2 h (◆: PbCl₂, ●: TiO₂, ▲: PbTiO₃).

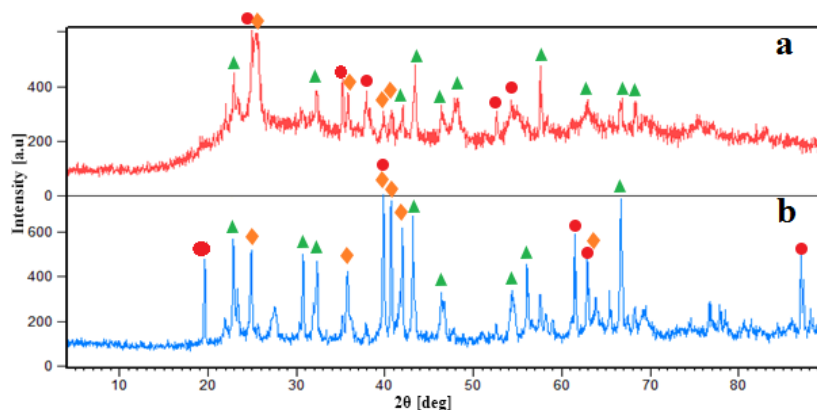


Fig. 3. XRD of the samples was maintained in an autoclave at 240 °C for 2 h, and in the furnace at 500 °C for 1 h. The hydrothermal reactions were carried out in a) ethanol, b) in water (◆: PbCl₂, ●: TiO₂, ▲: PbTiO₃).

in Table 2. The negative amount of the Gibbs free energy shows the reactivity of the reaction at room temperature.

X-ray diffraction (XRD) was used for investigation of the phase development and determining the mean size of nanocrystallites.

The peaks of PbCl₂ and TiO₂ can be observed in the peaks related to the samples that were kept in an autoclave at 180–240 °C (Fig. 2). The amount of lead titanate was increased by raising the temperature of

the autoclave. The samples 3 and 5 (Table 1) were heated in an autoclave at the same temperature, but they were prepared in different solvents. The XRD results (Fig. 3) show changing solvents will not impressively lead to an effect on the amount of lead titanate, even if the sample 5 heated up in furnace at 500 °C for 1 h. Also, by comparing the specimens 4 and 5, it can be concluded that the impurities are fewer when the reaction was carried out in ethanol. Besides that, water was not a proper solution for

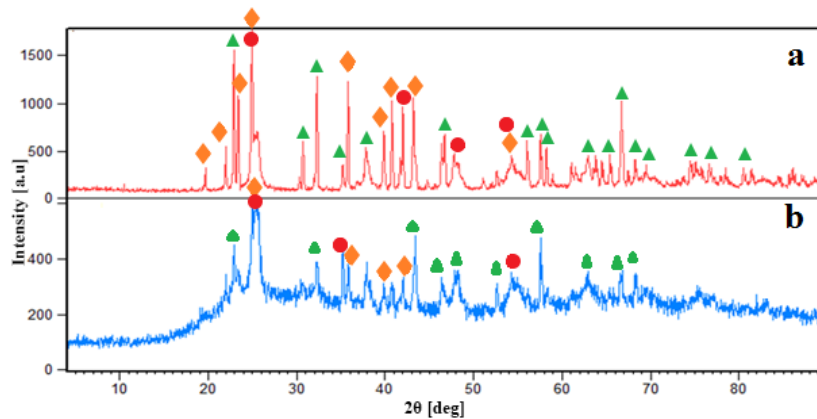


Fig. 4. XRD of the samples was maintained in an autoclave at 220 °C; a) without calcination, b) calcination for 1h at 500 °C (◆: PbCl₂, ●: TiO₂, ▲: PbTiO₃).

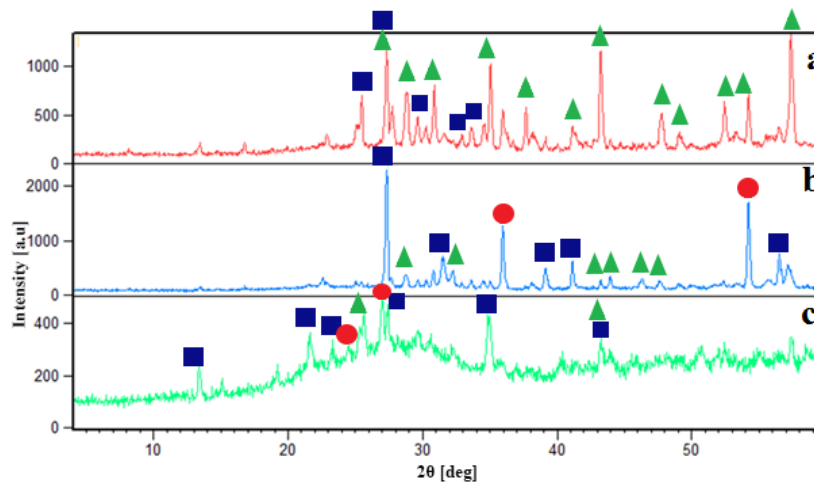


Fig. 5. XRD of the samples was maintained in an autoclave at 240 °C for 6 h and calcined at 900 °C for 6 h and prepared with different precursors; a) Pb(NO₃)₂ and TiCl₄, b) PbO and TiCl₄, c) Pb(NO₃)₂ and TiO₂ (■: PbTi₃O₇, ●: TiO₂, ▲: PbTiO₃).

titanium tetrachloride due to its extremely vigorous reaction with water.

In Fig. 4 the effect of the calcination on the development phase of the sample was maintained in an autoclave at 220 °C and then calcined for 1h at 500 °C was investigated. The secondary phases were decreased after the calcination and the intensity of PbTiO₃ was developed. In order to decrease the secondary phases, increasing the temperature of calcination is necessary which were carried out in samples 6, 7 and 8. The XRD analysis of these samples was shown in Fig. 5. The precursors for the synthesis of these samples are different. The secondary phases are fewer in sample 6 which was prepared by Pb(NO₃)₂ and TiCl₄, than the samples 7 and 8 which are synthesized by PbO, TiCl₄ and

Pb(NO₃)₂, TiO₂, respectively. The high volatility of Pb can lead to the formation of the secondary phases [16]. Therefore, the volatility of lead was less when the lead titanate made from lead nitrate and titanium tetrachloride. Thus, the next samples were prepared with these precursors.

Fig. 6 shows the XRD of the samples 1 and 11 which were prepared without calcination and with calcination. The sample 1 (Fig. 6a) was heated only in an autoclave at 180 °C for 2 h but the sample 11 (Fig. 6b) was heated in an autoclave at 180 °C and subsequently in the furnace for 8 h at 1200 °C. The difference in their peaks was completely recognizable. There are not any secondary phases in sample 11 and the synthesis was completed.

Sample 5 and 10 had the same condition in

Table 3: Crystallite sizes of the lead titanate samples which prepared according the condition was mentioned in Table 1.

Sample	D (nm)
1	6
2	7
3	7
4	7
5	8
6	8
7	8
8	9
9	8
10	7
11	10

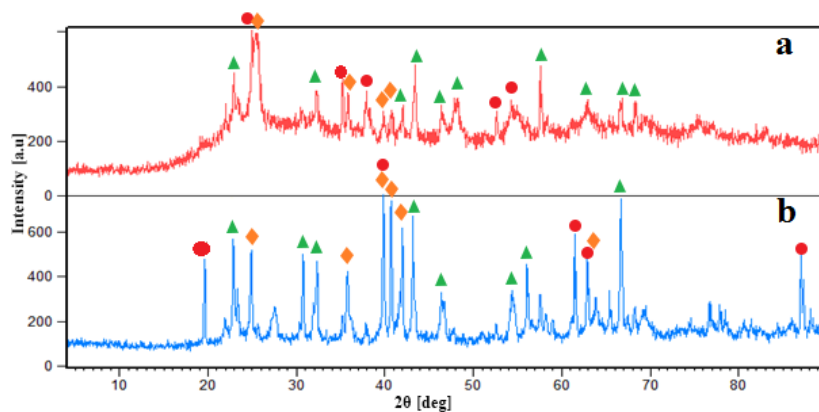


Fig. 6. XRD of the samples was maintained in an autoclave at 180 °C for 2 h, a) without calcination, b) calcined at 1200 °C for 8 h (◆ : PbCl₂, ●: TiO₂, ▲: PbTiO₃).

an autoclave. They were made from the same precursors with water. The XRD of these samples were shown in Fig. 7. Sample 5 was calcined at 500 °C for 1 h (Fig. 7a) and sample 10 was calcined at 1200 °C for 8 h (Fig. 7b). When the sample was heated in a furnace at a higher temperature for a longer time, the secondary phases were decreased or disappeared. The only phase in sample 10 is lead titanate.

Fig. 8 shows the XRD peaks of the samples 4, 6 and 9. By comparing the peaks of these samples, it can be concluded that the secondary phases are decreased by increasing the temperature at 1200 °C, the only formed phase is lead titanate (Fig. 8c) and the amount of the secondary phases are fewer in sample 6 (Fig. 8b) than sample 4 (Fig. 8a) because of heat treatment at a higher temperature and longer period.

The crystallite size of all specimens was summarized in Table 1. The measurements were done according to the Scherrer formula (1). The hydrothermal process led to the nanostructures. It seems that heating in the furnace in a longer period and higher temperature could affect the size of the crystallites. The heat treatment for a longer time at higher temperatures promoted the crystals to grow up because of the mechanism of seed and growth that can be observed in TEM.

Scanning electron microscopy (SEM) and transmission electron microscopy were carried out for investigation of the powders' morphology. Therefore, the specimens 2, 4, 5, 6 and 9 were selected for this purpose. Sample preparations are essential in scanning electron microscopy. For this purpose, first the samples were mixed with 10 cc acetone and dispersed ultrasonically. Then, a drop

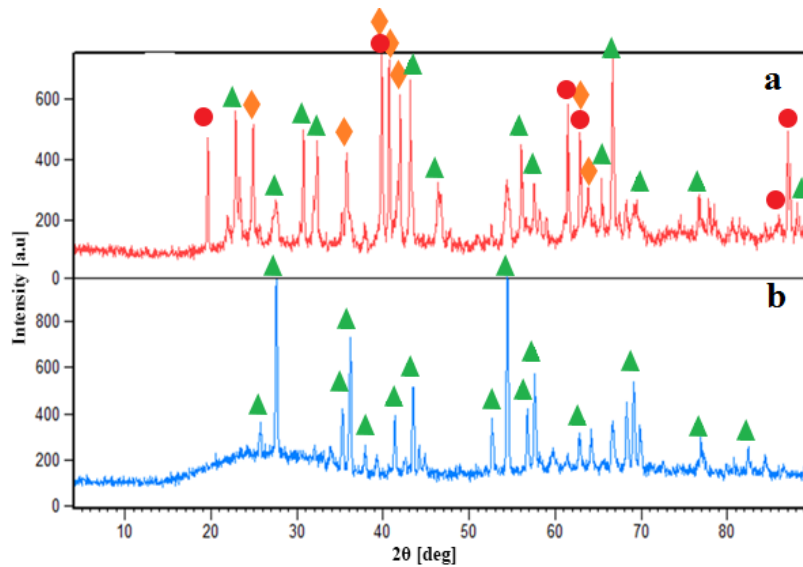


Fig. 7. XRD of the samples was made with water in an autoclave at 240 °C for 6 h, a) at 500 °C for 1 h and b) 1200 °C for 8 h (◆: PbCl₂, ●: TiO₂, ▲: PbTiO₃).

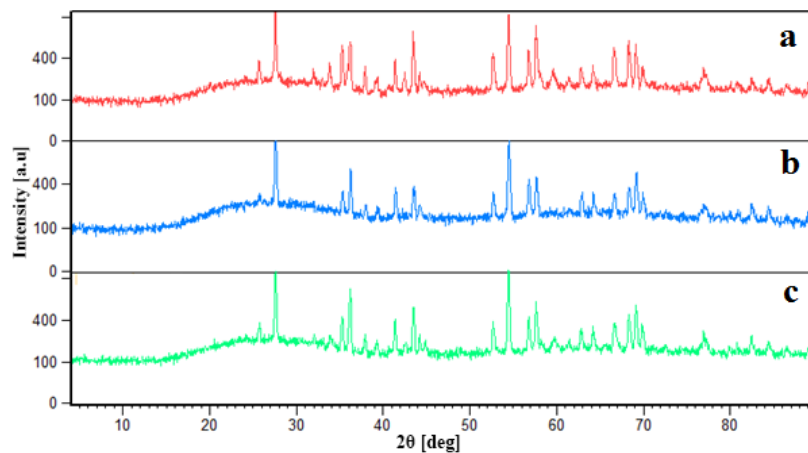


Fig. 8. XRD of the samples was calcined a) at 500 °C for 1 h, b) at 900 °C for 6 h and c) 1200 °C for 8 h (The peaks are related to PbTiO₃).

of suspension was placed in the center of the glass slide and then covered with a thin layer of gold.

Fig. 9 presents the SEM images of the selected samples. The grain size was increased first at 500 °C, however, the morphology structure and the growth did not change significantly at 900 °C. To complete the synthesis process, the temperature was raised to 1200 °C. Fig. 9a shows that heating of the sample for 8 h at 1200 °C can develop the grain growth compare to the sample which was heated for 6 h at 900 °C (Fig. 9b).

It is believed that small particles might have

greater reactivity potential and that may cause agglomeration. The mechanism for the formation of the PbTiO₃ particles is believed to involve dissolution and recrystallization of the poorly organized precursor into the cubic or platelet perovskite PbTiO₃ [23]. The nanoparticles were obtained and distributed in the sample. The pure phase of lead titanate with a perovskite structure can be observed. The rod-like morphology was created in some parts. Mudinepalli et al. found the ferroelectric hysteresis loops change significantly with grain size [27]. So, it can be concluded that the

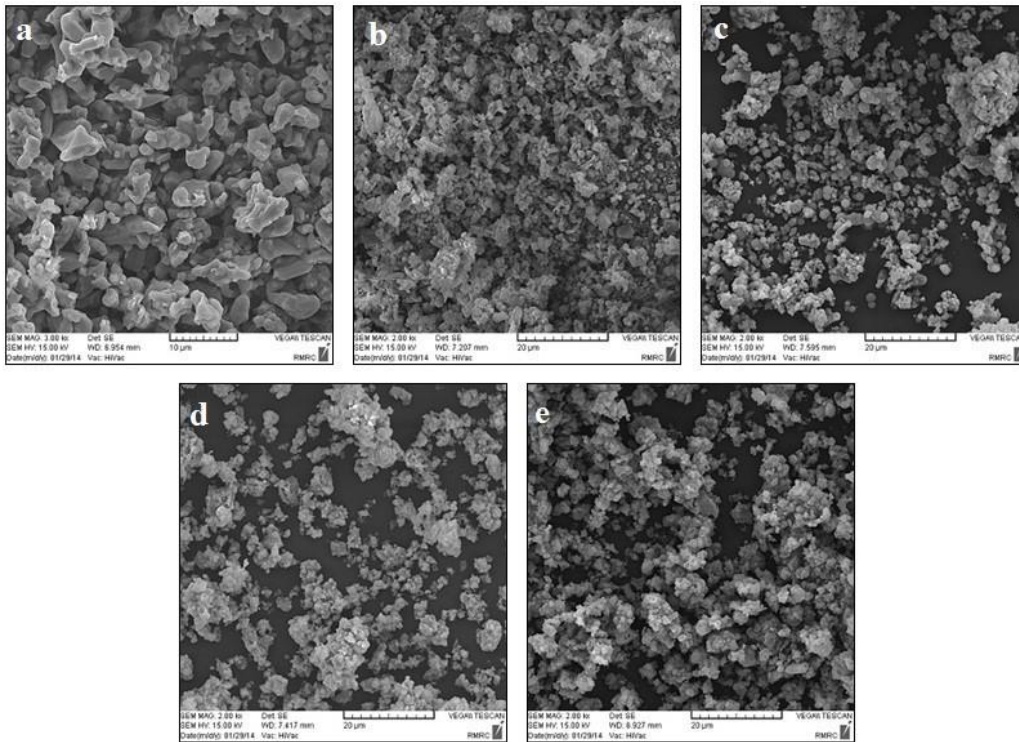


Fig. 9. SEM images of the specimens a) sample 9, b) sample 6, c) sample 4, d) sample 5 and e) sample 2.

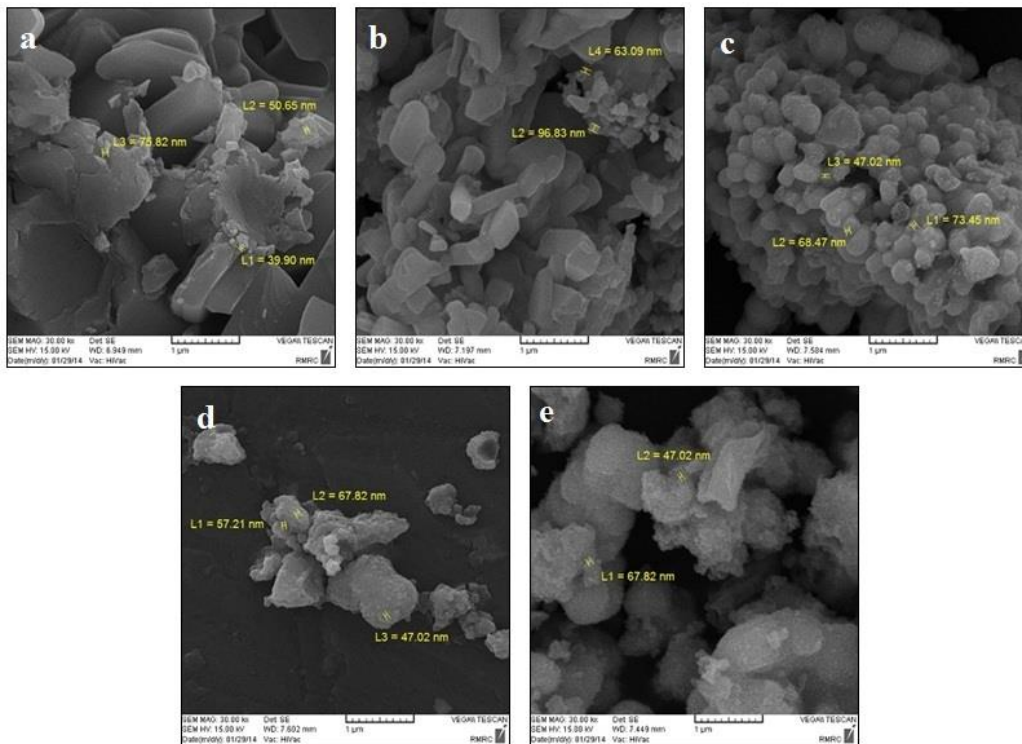


Fig. 10. SEM images of the specimens a) sample 9, b) sample 6, c) sample 4, d) sample 5 and e) sample 2.

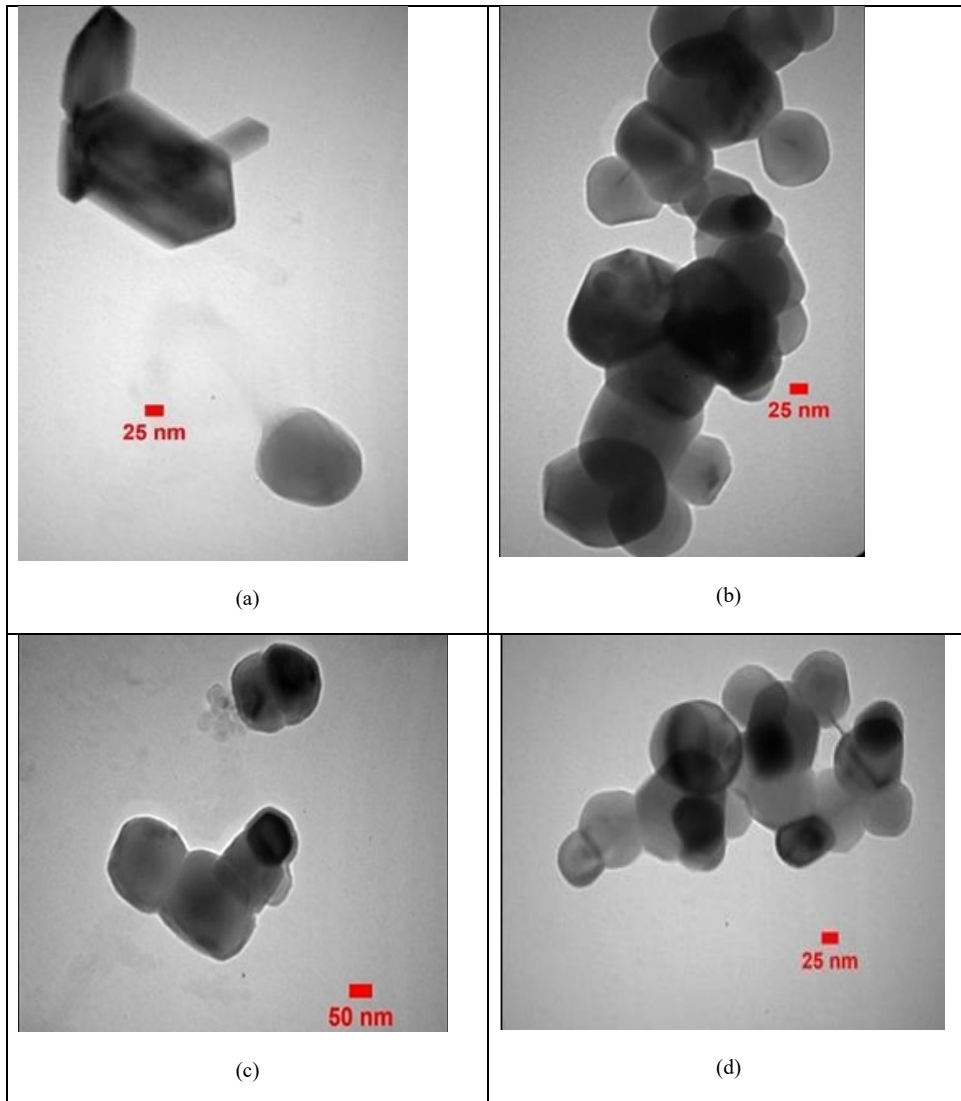


Fig. 11. TEM images of the samples a) calcined at 1200 °C for 8 h (sample 9), b) calcined at 500 °C for 1 h (sample 4).

samples were heated at 1200 °C (9,10,11) had the larger grains and ferroelectric domains that may cause a reduction of the dielectric constant.

Fig. 9d,e related to the lead titanate sample without sintering. These samples have spherical morphology with a narrow size and uniform morphology which can prepare powders with high sinterability property. The nucleation of the hydrothermal method generates particles. Therefore, it can produce the crystals with high quality, and uniform in morphology which can make the powder.

The agglomeration can be observed in the powders (Fig. 10). High surface area to volume ratio

of nanoparticles provides very high surface energy that can create agglomeration. It is because of van der Waals forces between the particles. The particle size is in nanometric scales, but the comparing of the particle size could not be measured precisely because of the agglomeration.

Fig. 11 shows the transmission electron microscopy (TEM) images of the samples 4 and 9 which calcined in the furnace at 1200 °C for 8 h and 500 °C for 1 h, respectively. The heat treatment for a longer time at higher temperatures promoted the crystals to grow up because of the mechanism of seed and growth. The lead titanate was crystallized completely at high temperature and the perovskite

hexagonal structure of this sample is presented in Fig. 11a. The size of this sample is around 100 nm. The powder at 500 °C has the spherical morphology and at higher temperatures, the crystals grow up in the direction of the h-axis. The agglomeration was created between the particles due to very high surface energy and the van der Waals forces between the particles that were revealed in SEM images, too.

CONCLUSION

A hydrothermal method has been carried out to prepare PbTiO₃ powders successfully. The results of this research are summarized:

- 1- The particles had a spherical morphology at a lower temperature, but perovskite hexagonal structure at a higher temperature.
- 2- The volatility of lead was prevented by the hydrothermal method.
- 3- The lead titanate crystals were completed at 1200 °C.
- 4- The hydrothermal synthesis was caused by stoichiometric PbTiO₃ nanopowders.
- 5- Heating in the furnace for a longer period and higher temperature could affect the size of the crystallites.
- 6- The powder was heated at 1200 °C had larger grains and ferroelectric domains that may cause the reduction of the dielectric constant.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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