

## **Synthesis and Characterization of PbTiO<sub>3</sub> Nanopowders by Citric Acid Gel Method**

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### **ABSTRACT**

High purity lead titanate nanopowders in tetragonal form have been successfully prepared by citric acid gel method using lead nitrate and tetra-n-butyl titanate as Pb and Ti sources respectively and citric acid as complexing reagent. The precursors were calcined at various temperatures ranging from 450 °C to 600 °C for 2 h. Fourier Transform Infrared Spectroscopy (FT-IR), X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) were used to characterize the crystallization process, particle size and morphology of the calcined powders. The results indicated that lead titanate nanoparticles with an average size ranging from 35-50 nm could be obtained after calcining of the dried gel at 550°C for 2 h.

**Keywords:** Lead titanate nanopowders; Sol–gel synthesis; Citric acid gel method; Transmission electron microscopy

### **INTRODUCTION**

Lead titanate (PbTiO<sub>3</sub>) is a promising ferroelectric material and has been the focus of much attention for various device applications, such as non-volatile memories, actuators and transducers due to their excellent piezoelectric and electrooptic properties. It shows an order of magnitude lower dielectric constant (~200) compared to barium titanate and PZT ceramics, a high curie point of ~490 °C [1-4]. Many methods have been applied to prepare lead titanate powders, such as sol–gel method [5-11], co-precipitation [12-17] and hydrothermal synthesis [18-25], besides the traditional solid-state reaction of mixed oxides [26]. It is widely recognized that chemical synthesis methods are able to provide high

chemical purity, precise composition, uniform microstructure and a lower formation temperature of the perovskite phase based on molecular scale mixing in the preparation of the precursor. The sol–gel route is proved to be a very commonly applied chemical method for fabricating uniform large area thin films and synthesizing powders of micrometer, sub-micrometer, or nanometer size with high purity and homogeneity. Furthermore, the morphology of the particles could be easily controlled by changing the synthesis parameters [27-30].

In this paper, we focus on a sol–gel synthesis method of PbTiO<sub>3</sub> based on a metal–citrate complex system reported recently. This method herein offers an easy route to control the final

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stoichiometry of  $\text{PbTiO}_3$  composition and lead to the uniform nanopowders.

## EXPERIMENTAL

$\text{PbTiO}_3$  powders were synthesized by a complex precursor route as summarized in Fig. 1. Citric acid (99.5+ %), tetra-n-butyl titanate,  $\text{Ti}(\text{n-OC}_4\text{H}_9)_4$  (98+%),  $\text{H}_2\text{O}_2$  (30 wt.% in  $\text{H}_2\text{O}$ ),  $\text{Pb}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (98%), and ammonia solution (25–28 wt.% in  $\text{H}_2\text{O}$ ) were employed as the starting ingredients.  $\text{Ti}(\text{n-OC}_4\text{H}_9)_4$  was added to stirred deionized water, the precipitation and turbidity were observed gradually, then the precipitate was filtered and washed for several times with deionized water. Citric acid and  $\text{H}_2\text{O}_2$ , both in a 2:1 molar ratio against  $\text{Ti}(\text{n-OC}_4\text{H}_9)_4$ , were added. With the addition of these ingredients, the solution became maroon in color and viscous. The pH value of the solution was adjusted to 6 using ammonia solution. A water-soluble precursor for Ti(IV) was prepared with continuous stirring and refluxing at 60 °C. Then stoichiometric amount of  $\text{Pb}(\text{NO}_3)_2$  was dissolved in citric acid solution (5 M) with pH of 6, adjusted by ammonia solution with molar ratio of CA: Pb = 2:1 (CA, citric acid) and Pb(II) precursor was mixed with Ti(IV) precursor. The whole mixture was refluxed at 60 °C for 1–2 h with continuous stirring and then a porous citreous resin was formed after drying in a furnace at 60 °C overnight under flowing air for 2 h. This solid resin precursor was pulverized and then calcined at various temperatures for 2 h to obtain the  $\text{PbTiO}_3$  powders.

The FTIR spectrum was recorded with an MB100 (BOMEM) spectrometer by using KBr pellet. The XRD patterns of the powders were recorded on a Model PTS 3003 of SEIFERT diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) in the range from 10° to 60° (2 $\theta$ ) to examine the crystallization and structural development of  $\text{PbTiO}_3$  powders. The TEM picture was recorded with Philips Model EM with continuous stirring and then a porous 208 instrument at the accelerating voltage of 100 kV. The fine powders were dispersed in amyl acetate on a carbon coated TEM copper grid.

## RESULT AND DISCUSSION

Fig. 2 illustrates the FTIR spectra for  $\text{PbTiO}_3$  powders derived via the citric acid gel method and calcined at various temperatures ranging from

450 °C to 550 °C. The IR spectrum of the sample calcined at 450 °C clearly indicates the presence of Ti–O band characterized by the absorption

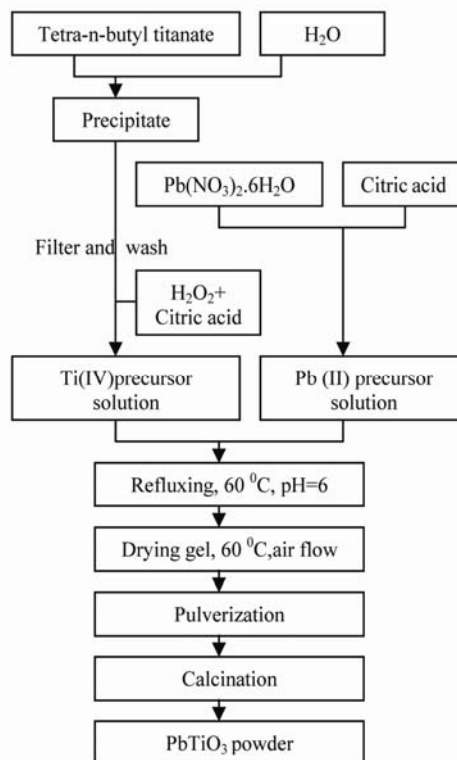


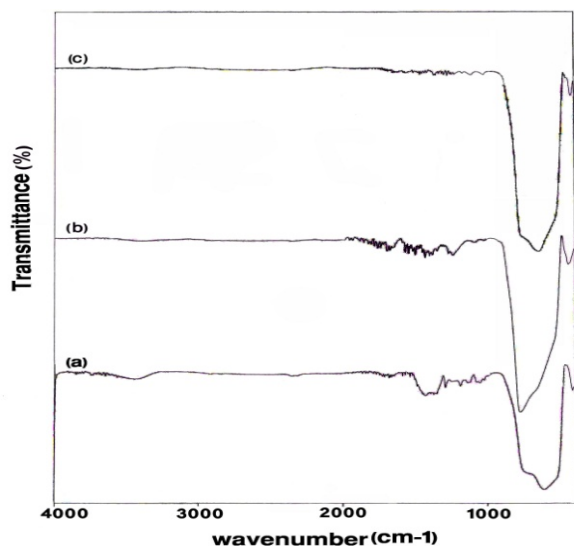
Fig. 1. Flowchart for the preparation of  $\text{PbTiO}_3$  nanopowders.

bands at 604, 726  $\text{cm}^{-1}$  [31]. The broad band at 3431  $\text{cm}^{-1}$  was assigned to stretching vibration of weakly bound water. It was reported that absorption bands over the range of 1000–1700  $\text{cm}^{-1}$  are mainly related to the organic groups [11]. Increasing the calcination temperature to 500 °C results in decrease in intensity of the organic absorption bands and increased intensity of the absorption Ti–O band. The organic residuals were completely eliminated when the derived powders were calcined at 550 °C and IR spectrum corresponding to  $\text{PbTiO}_3$  powders [31].

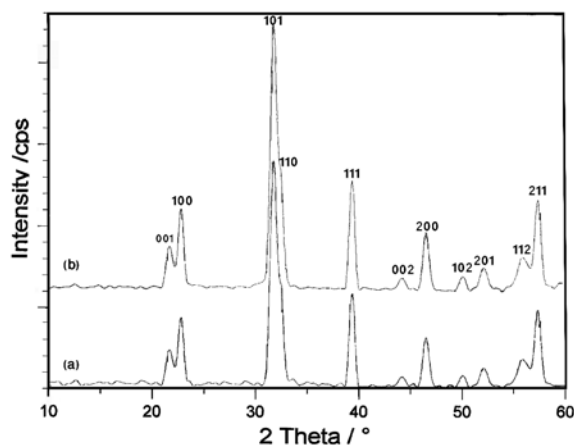
XRD pattern of the  $\text{PbTiO}_3$  calcined at 500 °C and 550 °C is shown in Fig. 3. At 500 °C, the crystallization of tetragonal lead titanate phase began along with traces impurity phase. At 550 °C all peaks can be indexed to the  $\text{PbTiO}_3$  with a tetragonal structure (JCPDS: 78-0299).

No peak corresponding to any of the source materials or allotropic forms was found, suggesting that a pure crystalline compound exists. This is the lowest temperature which has

been reported so far for the formation of  $\text{PbTiO}_3$  by the citric acid gel method. 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,  $k=0.9$ ,



**Fig. 2.** FT-IR spectra of the powders calcined at (a) 450 °C; (b) 500 °C and (c) 550 °C.



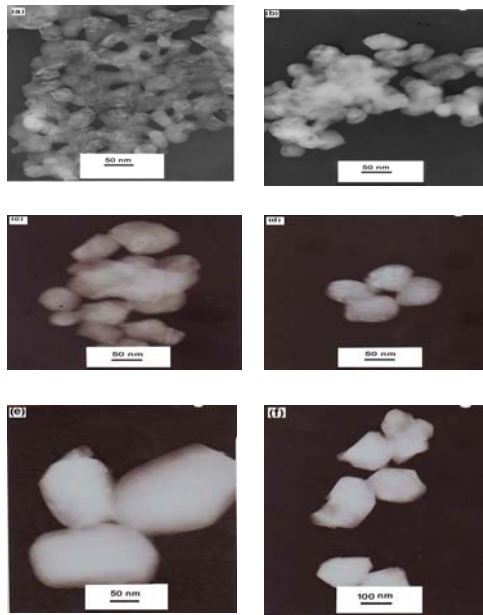
**Fig. 3.** XRD pattern of the  $\text{PbTiO}_3$  calcined at (a) 500 °C and (b) 550 °C for 2 h.

$\lambda$  is the wavelength of X-ray radiation,  $\beta$  is the full width at half maximum of the diffracted peak and  $\theta$  is the angle of diffraction. The crystallite size obtained from XRD data at 500, 550 °C were 30.28 and 39.25 nm, respectively.

Fig. 4 shows the TEM images of  $\text{PbTiO}_3$  powders prepared by citric acid gel method after calcination from 500 °C to 600 °C for 2 h. The crystallite size obtained from XRD data was shown in table 1.

**Table 1**  
Crystallite size in the TEM images

Temperature (°C)	500	550	600
Crystallite size (nm)	35-65	35-90	130-190



**Fig. 4.** TEM images of  $\text{PbTiO}_3$  nanopowders calcined at (a),(b) 500 °C; (c) ,(d) 550 °C and (e), (f) 600 °C for 2 h.

At 500 °C, the size of particle is not consistent with the XRD results calculated by Scherrer formula (see Table 1). It indicates that most of crystallites of  $\text{PbTiO}_3$  adhere together and form large particles. At 550 °C the grain size is consistent with the XRD results calculated by Scherrer formula. By increasing the calcination temperature to 600 °C the particle size was increased (see Table 1).

## CONCLUSION

Lead titanate nanopowders have been synthesized by the citric acid gel method using citric acid as complexing reagent. High Purity tetragonal phase  $\text{PbTiO}_3$  with perovskite structure was formed at 550 °C. This is the lowest temperature reported so far for the formation of  $\text{PbTiO}_3$  by the citric acid gel method. The calcined powders showed most particles are fine and their sizes were estimated with the ranging from 35-90 nm, a value consistent with the one calculated by the XRD data. The particles size was increased by increasing the calcination temperature.

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