

Article

Novel Sol-Gel Synthesis of Spherical Lead Titanate Submicrometer Powders

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Abstract: In this study, a novel and simple synthetic sol-gel procedure was established to directly prepare spherical lead titanate powders without prior synthesis/usage of spherical templates such as TiO₂ particles. Isotropic submicron particles with a mean diameter of 1–4 μm were prepared in this way. This synthetic process takes advantage of acetone as a stabilizing ligand and autogenous pressure generated in the autoclave during the reaction. The influence of various experimental factors (nature of the ligand, thermal treatment mode, and post-calcining temperature) as well as the formation mechanism were studied. Scanning electron microscopy and transmission electron microscopy were used to explore the particle morphology. The crystalline phases were explored and identified by X-ray diffraction analysis.

Keywords: lead titanate; powder; spherical particles

1. Introduction

Lead titanate (PbTiO₃, PT) is a key ferroelectric compound with various technological applications which cover the field of electro-ceramics. This material has a high Curie temperature (approximately 490 °C), high spontaneous polarization, and large pyroelectric coefficient. Lead titanate has been extensively employed as a material for functional ceramic for ultrasonic transducer, optoelectrical devices, and capacitors on account of its dielectric, pyroelectric, and piezoelectric properties. The control of the microstructure, its morphology, particles size, and monodispersity are key parameters for a successful synthesis of PT powders.

Nanostructure materials have exceptional physical properties and vast application areas. Therefore, the development of new techniques for the synthesis of particles with nanoscopic dimensions and well-defined shapes is currently a driving force for research. Several representative papers concerning properties and applications of nanomaterials were reported [1–5]. Several techniques have been tried for the synthesis of pure, homogeneous, and fine lead titanate powders. Many configurations and parameters have been varied, even within a single method, in order to prepare un-agglomerated powders with restricted size distribution interval. Common methods for preparing nano-sized PT fine powders comprise chemical co-precipitation, sol-gel and hydrothermal synthesis, in addition to the

conventional solid-state route of mixed oxides. The majority of these techniques necessitate relatively high calcination temperatures to transform the PT amorphous powders into a single-phase ferroelectric material. This accentuates the particle aggregation, which results in unaccomplished sintering. The particles will possibly get through the Curie temperature, which may result in residual strain following the phase transition. Moreover, most of the powder processing procedures fail to produce well-defined and finely dispersed particles, which are essential in the manufacturing of high-performance devices.

It has been established that the size and shape of a powder are very important factors, which influence the material properties. In particular, the hydrothermal process has been successfully used to form PT powders with acicular [6,7], cubic [8–10], fibrous [11], nanowires [12], and plate [13], tubular [14] shapes. However, it is difficult to directly produce spherical PT powder due to the intrinsic formation behavior [15]. Spherical and nanometer-sized powders are particularly required for the sintering of highly dense ceramics [16]. Choi et al. [15] have used hydrothermally prepared spherical TiO_2 gel particles [17] to synthesize lead titanate. The TiO_2 gel powders were subsequently reacted with lead acetate trihydrate in a stainless-steel autoclave with Teflon liner. The lead titanate produced powders acquired the spherical shape. In a similar manner, Cai et al. [18] used an analytically grade reagent of TiO_2 with spherical shape as a titanium source to prepare the same compound using molten-salt synthesis. The lead ions diffused through the surface of TiO_2 with the formation of PbTiO_3 . The formation of spherical PT powder was interpreted in terms of a template formation mechanism. The quality of the particles developed by the above methods is very sensitive to many processing factors such as pH, temperature, and reactant concentrations.

It becomes clear from the above exposition that the prior preparation of TiO_2 is the essential step towards the successful synthesis of PT spherical particles. The original shape and size of TiO_2 particles defined the final shape as well as the size of the PT product. Furthermore, the introduction of alkali cations such as Na^+ and K^+ , which are introduced during hydrothermal processing, may affect the ferroelectric and the electrothermal properties of the final product. The negative effects of alkali ions on lead zirconium titanate (PZT) were reported [9,14,15,19–23]. However, to the best of our knowledge, there is no scientific report on the synthesis of well-defined PT spherical particles without using TiO_2 seed grains of a specified shape.

Chemical methods have engendered great attention for the production of an ABO_3 form of oxide powders with small particle size and high purity. Sol-gel technology is among the simplest procedures for the preparation of high purity, stoichiometric, fine particles of various multicomponent oxides. This article presents some interesting results related to the formation of PT nano-spheres. Its main objective is to demonstrate that spherical PT powders can be produced via sol-gel procedure in one step, and without using any template or surfactant.

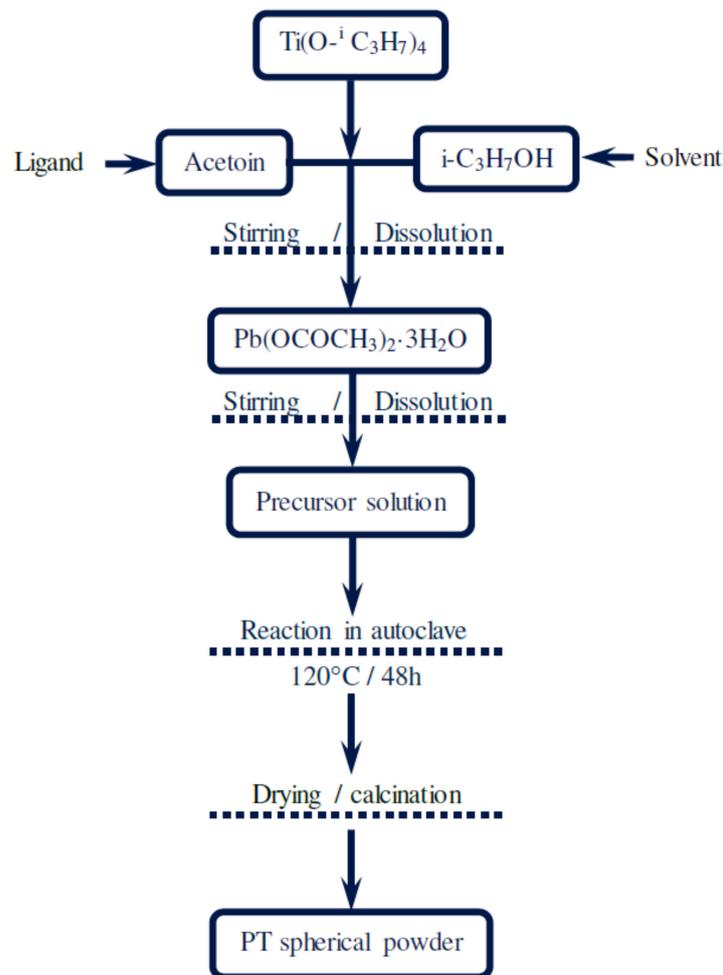
2. Experimental Section

Lead acetate trihydrate [$\text{Pb}(\text{OCOCH}_3)_2 \cdot 3\text{H}_2\text{O}$] (99%, Aldrich, Munich, Germany), isopropanol [$(\text{CH}_3)_2\text{CHOH}$] (99.5%, Aldrich, Munich, Germany), acetoin [$\text{CH}_3\text{COCH}(\text{OH})\text{CH}_3$] (Aldrich, Munich, Germany), and titanium (IV) isopropoxide [$\text{Ti}(\text{OC}_3\text{H}_7)_4$] (97%, Aldrich, Munich, Germany) were used as raw materials. Transition-metal alkoxides are very sensitive, and hydrolysis and condensation occur rapidly in the presence of water. Hence, the control of these reactions is essential in multicomponent precursor systems. Therefore, the starting solution was prepared by dissolving titanium (IV) isopropoxide into isopropanol using acetoin (2 mol with respect to the Ti ions) as a chelating ligand. Equivalent amount of lead acetate trihydrate was then added under mild agitation at RT until complete dissolution. All reactions were carried out under a dry nitrogen environment. The initially turbid yellow solution became clear within one hour. The main characteristics of the solution are listed in Table 1.

Table 1. Characteristics of the precursor solution.

Metal Concentration (mol/L)	Molar Ratio	Appearance	Stability
0.4	Acetoin:Ti = 2 Pb:Ti = 1	Yellow	About 6 months

The reaction mixture was sealed in a stainless steel autoclave with 80% filling factor. The reaction was conducted at 120 °C for 48 h under autogenous pressure without being magnetically stirred. The vessel was finally cooled under recycling water to RT. An orange precipitate formed. The solid precipitate was recovered by filtration, dried at 120 °C for 48 h, and ground in a mortar. The detailed procedure is schematically described in Figure 1.

**Figure 1.** Flow chart of the preparation steps of PT powder.

As shown in this figure, we illustrate a simple process to produce unique PT particles at mild conditions (120 °C without using any polymers or surfactants).

The morphology, size, and composition of PT particles were explored with scanning electron microscopy (SEM, Joel Model 6360 LVSEM, Akishima, Tokyo, Japan) equipped with Energy-Dispersive X-ray spectrometer (EDX). Selected samples were also analyzed by transmission electron microscopy (TEM, JEM-2100F). Powder X-ray diffraction (XRD, Model RAD-2R, Rigaku Co., Tokyo, Japan) was used to analyze the crystallization behavior of the PT powders. X-ray diffractograms were recorded at room temperature in reflection mode with CuK α radiation (40 kV, 30 mA). The measurements were performed in a step mode (2° / min), from 10° to 80° in 2 θ .

3. Results and Discussion

3.1. Morphology of PbTiO_3 Powders

A combination of TEM and SEM techniques was used to explore the morphological evolution and particle size evaluation. The morphologies of the as-prepared powders are displayed in Figure 2.

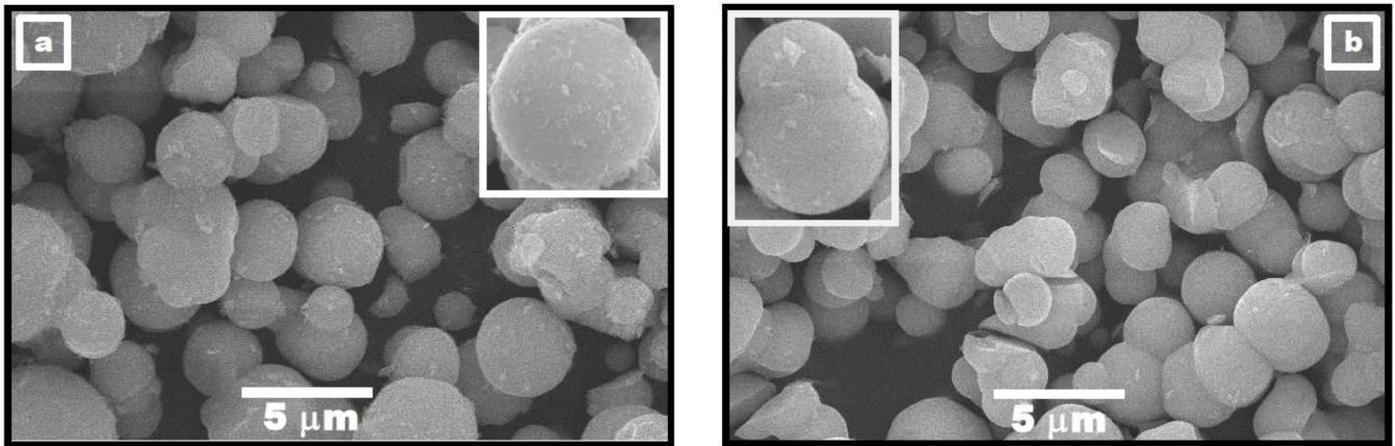


Figure 2. SEM micrographs of PT gel powders: (a) as made and (b) dried at 120 °C for 48 h.

Spherical and uniform particles with size in the range of 2–5 μm formed under the double effects of autogenous pressure and temperature. The particle surface is smooth and has no convexity or concavity (inset Figure 2a). The spherical shape of the particulates is in contrast with other conventional routes [6–14], where other forms are produced. Few adjacent sub-micron-particles fused gradually, as the reaction time increases (Figure 2b), but the morphology was not significantly affected. The precursor system reacted at temperatures higher than 120 °C (up to 180 °C), but this did not result in a significant change in particle morphology and size. Furthermore, the as-prepared powder conserved their spherical morphology after the post-calcining process. The SEM images of the PT gel powder calcined at various temperatures were similar. The typical image relative to PT powder annealed at 350 °C for 10 h and is shown in Figure 3.

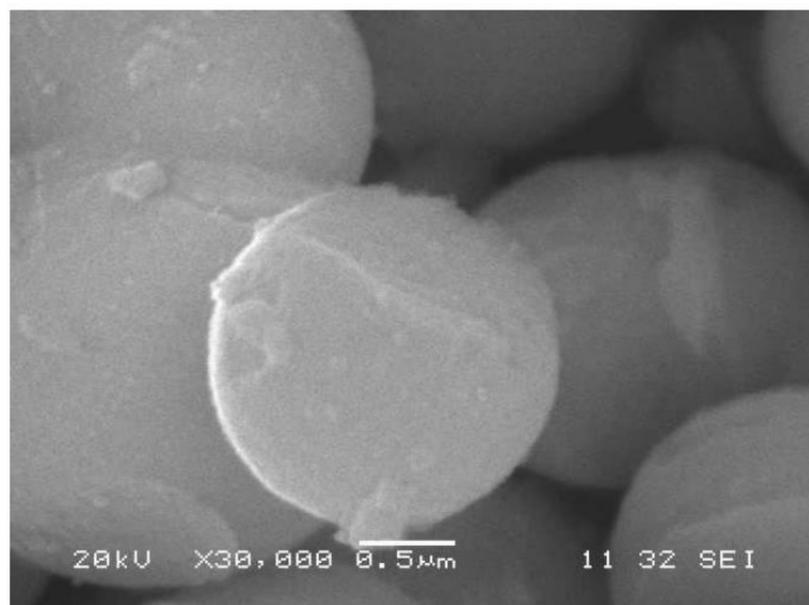


Figure 3. SEM micrograph of PT powder calcined at 350 °C for 10 h.

This synthetic procedure has shown a high level of reproducibility. In contrast, several reported research work [24,25] revealed that the particle morphology is strongly dependent on the calcination temperature for ferroelectric compounds processed via other chemical routes.

In order to get more insight on the growth mechanism, we performed the reaction under different parameters. At first, we prepared the PT powder by drying the solution at 50 °C and subsequently heated the obtained powder at 120 °C for 48 h at atmospheric pressure outside the autoclave. The particles followed a different morphological growth route as displayed in Figure 4.

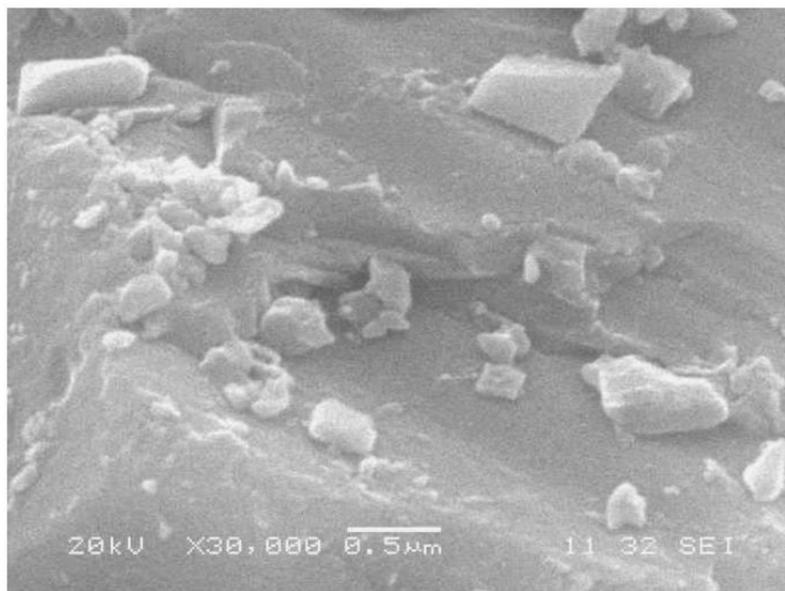


Figure 4. SEM micrograph of powder obtained at 120 °C for 48 h at atmospheric pressure. The reaction took place outside the autoclave.

Complex and irregularly shaped particles formed. This clearly demonstrates the important role of the autogenous pressure during the reaction in favoring the development of the spherical morphology.

With the intention of discovering the ensuing effect of the ligand on PT powder morphology, a second experiment was undertaken by incorporating diethanolamine (represents one candidate of alkanolamines, which is commonly used as a ligand in sol-gel processes) in the precursor solution instead of acetoin. The metallic compounds were allowed to react inside the autoclave and the same conditions were maintained. The dependence of the particulate morphology on the nature of the complexing ligand is obvious from Figure 5.

Featureless grains with an irregular shape were formed instead of the spherical morphology. Few particles showed geometrical morphology with sharp edges.

These experiments clearly demonstrate that in the present study, the reaction in the autoclave is an indispensable step to produce spherical PT particles. The important role of acetoin is probably due to the enhanced nucleation rate.

Semiquantitative EDX measurement revealed that lead and titanium were the only metals present (Figure 6).

About 6 mass % of carbon remained in the sample after calcination at 450 °C for 4 h. Higher firing temperature and/or longer duration are needed to completely oxidize the carbon. The EDX spectrum of the PT gel powder shows that the Pb:Ti ratio approximating 0.93 is slightly smaller than the nominal ratio of the perovskite. The eminent adverse effect of lead loss during PT processing is classically bypassed by providing excess lead in the starting composition. Generally, lead hyper-stoichiometric compositions were found to crystallize at relatively lower temperatures than those deficient in PbO, irrespective of Zr/Ti proportion. In the present work, stoichiometric composition was used to synthesize

the precursor solution. Excess lead was reported to increase the possibility of the retention of PbO at grain boundaries or as a second phase [26–28]. This may adversely affect the electrical characteristics of the final material. Besides concerns related to lead toxicity, extensive degassing due to metallic lead and/or lead oxide vaporization may leave voids causing less dense product.

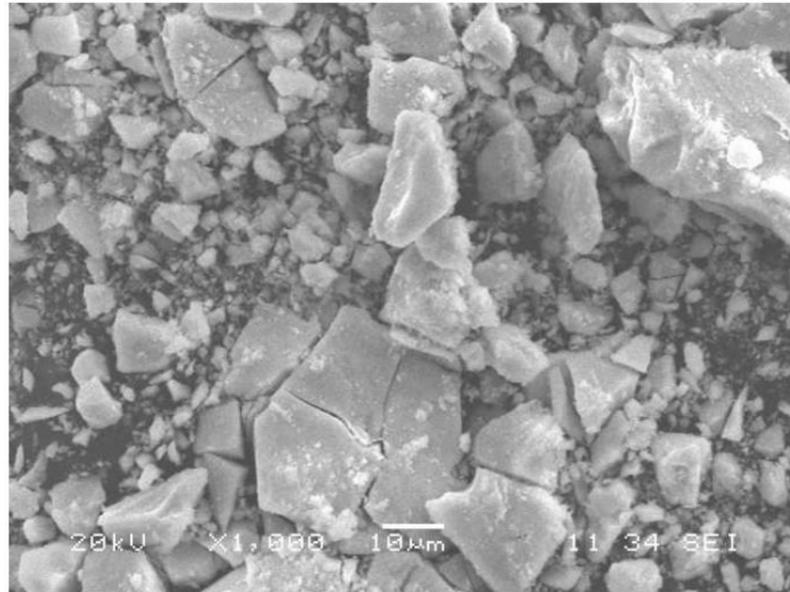


Figure 5. SEM micrograph of powder synthesized at 120 °C for 48 h from the solution prepared using diethanolamine.

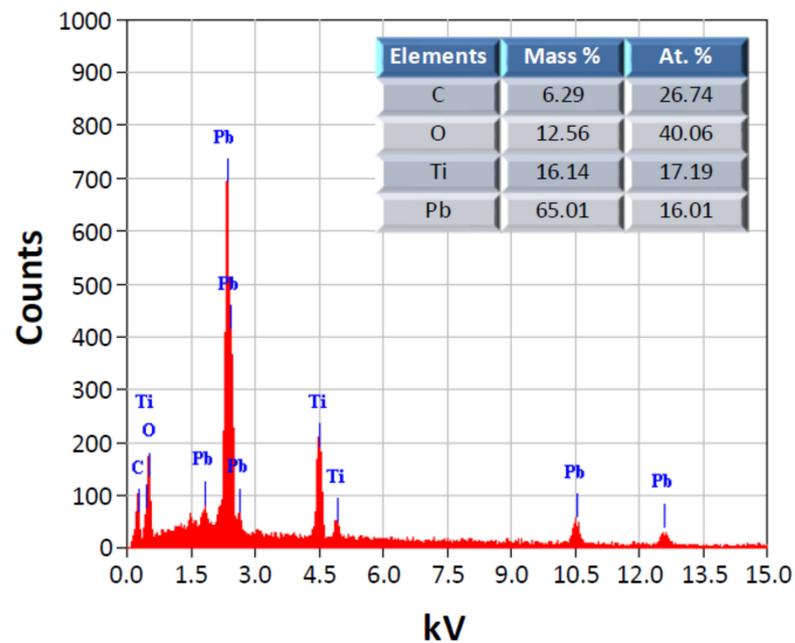


Figure 6. EDX spectrum of PT gel powder calcined at 450 °C for 4 h.

The TEM analysis has been conducted as complementary structural analysis. The TEM micrographs shown in Figure 7 confirmed the perfectly spherical shape of the PT primary particle and demonstrated that it was composed of nanometric sub-particles (Figure 7b), with an average particle diameter of about 1 nm. The outlines of the surficial nanoparticles are clear, and their size distribution is expected to be narrow. Overall, this distinctive spherical compartment will guarantee a high sintered density and homogeneous

microstructure for lead titanate ceramic at a low sintering temperature. The nanoparticle size distribution was measured in the TEM (Figure 8a) and the resulting size distribution is shown in Figure 8b. The average size and standard deviation were calculated to be 3.53 ± 0.05 nm.

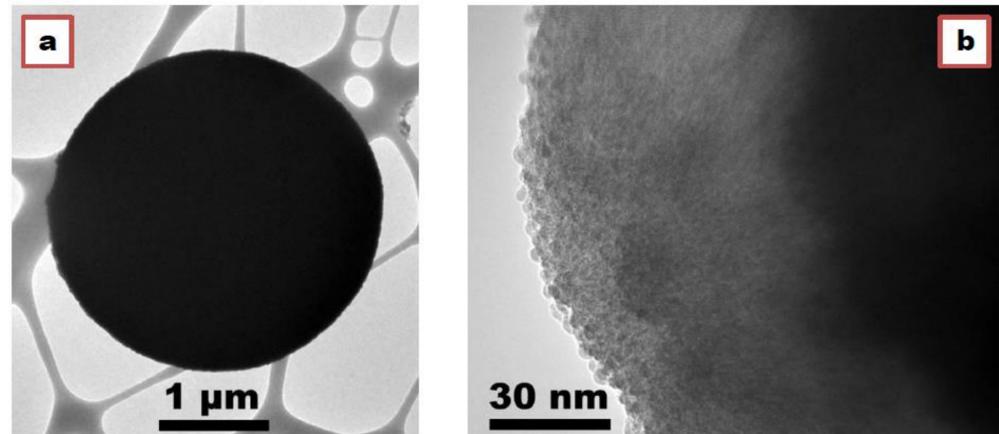


Figure 7. TEM micrographs of PT as made particle at (a) low and (b) high magnifications.

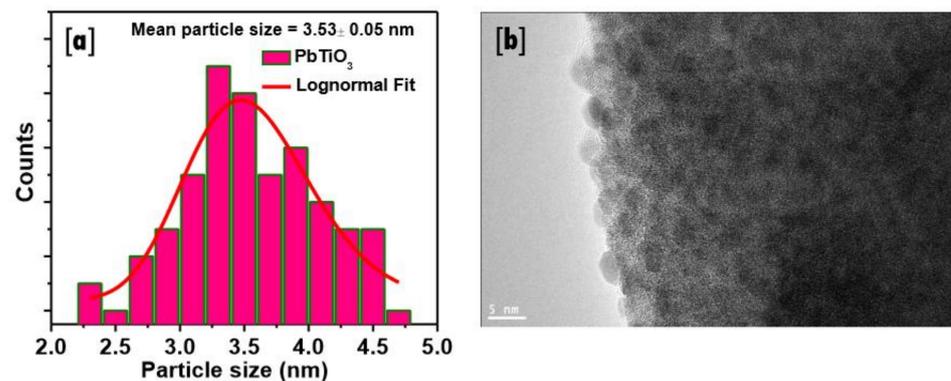


Figure 8. Size distribution of the as-made particles synthesized from the PT-AC system (a) and the corresponding TEM image (b).

The method developed in the present study enables the fabrication of well-shaped spherical PT particles composed of nanocrystals. The successful manufacturing of nanostructured PT powders is of great importance for device miniaturization, and it facilitates the integration of these powders within electronic components. The synthesis of PT material through this approach may also provide a typical strategy for the production of other perovskite ceramic materials.

3.2. Crystalline Phase Development

The crystalline phases that developed upon calcination were analyzed by X-ray diffraction. The XRD spectra of the PT powders calcined at various temperatures and durations are superposed in Figure 9.

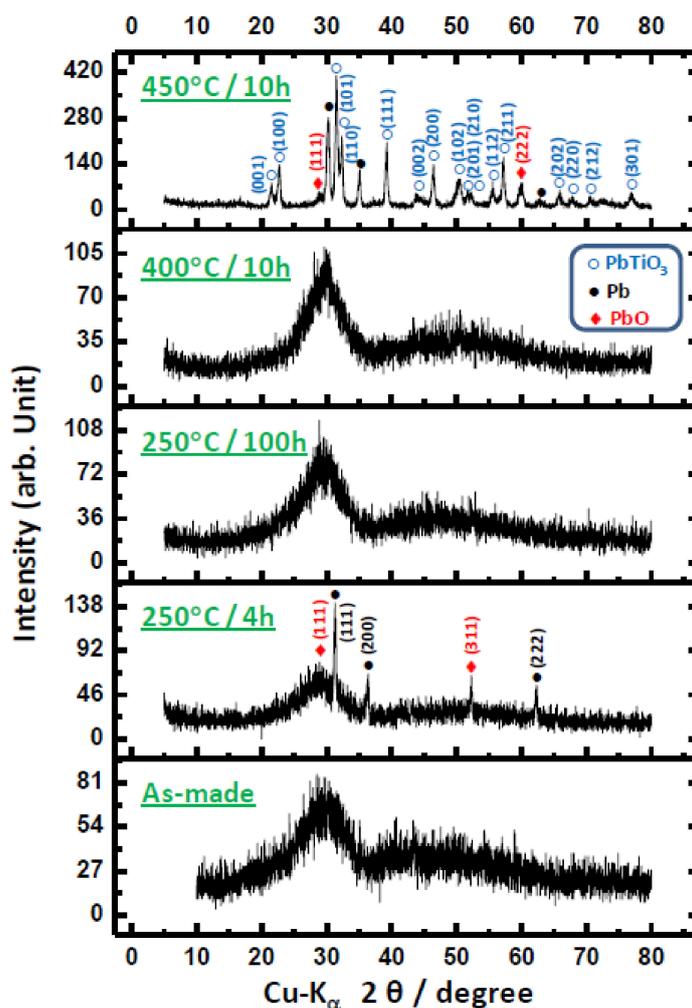


Figure 9. Powder XRD spectra of the PT powders calcined at various temperatures and dwell times.

The uncalcined powder is amorphous. A broad continuum pattern is detected, which points to the existence of a polymeric network holding different metal ions together. The decomposition of lead acetate started when the powder was calcined at 250 °C for 4 h. The X-ray reflections corresponding to metallic lead that existed in a free state appeared simultaneously with orthorhombic PbO (JCDPS 0771971). The metallic reduction was often reported in various chemical approaches [29]. Typically, chemical methodologies based on the use of organic molecules to stabilize the cations and circumvent early hydrolyses cause a local reducing atmosphere throughout the crystallization step because of the combustion of organic fraction. This explicates the formation of lead metal in the present case. Partitioning of metallic Pb and/or PbO during $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ powder pyrolysis was formerly observed [30]. The formation of metallic Pb was also confirmed by Li et al. [31] and by Budd et al. [32] in the XRD spectra of $\text{Pb}(\text{Zr}_{0.8}\text{Ti}_{0.2})\text{O}_3$ and PbZrO_3 powders, respectively.

The crystalline phases again disappeared at the expense of an amorphous phase when the dwell time of the calcination procedure was extended up to 100 h while maintaining the same temperature. The reaction between lead and titanate gradually proceeded as the calcination temperature/time was increased. The XRD plot of PT gel powder thermally treated at 400 °C revealed a broad peak suggestive of fine crystalline particles. The tetragonal PbTiO_3 perovskite structure started to form when the calcining temperature reached 450 °C. The reflections from unreacted metallic lead and lead oxide that were previously reported [33,34] are also detected. The non-ferroelectric pyrochlore intermediate phase was not detected during the entire thermal process. It is worth noting at this point that it was possible to form a single PT phase (see Figure 10) at an even lower temperature of 400 °C

from the PT-AC solution when it was not allowed to react in the autoclave. However, the obtained powder had irregular morphology.

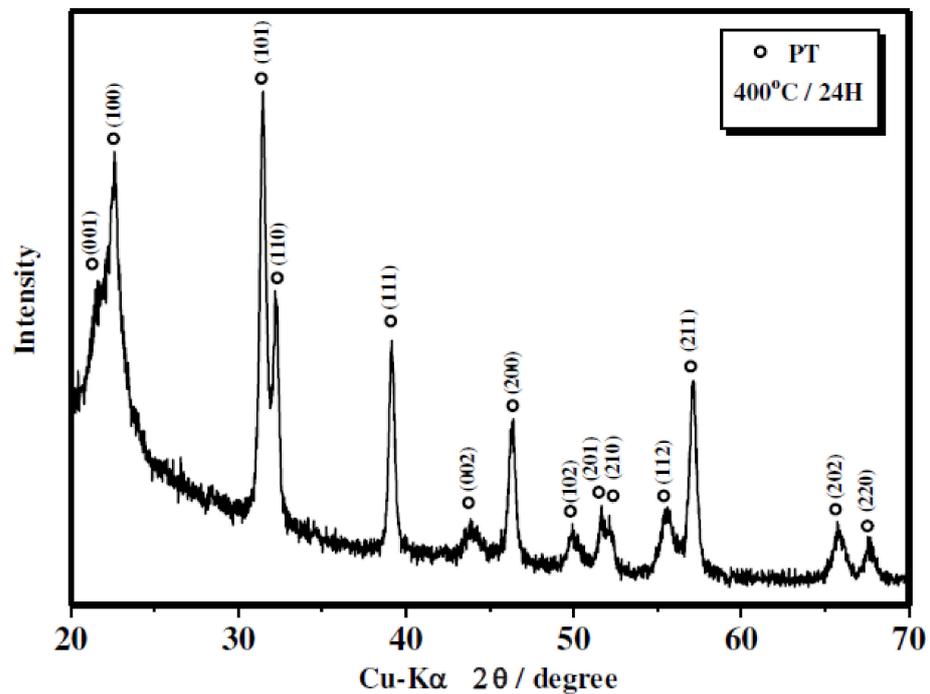


Figure 10. X-ray spectrum of PT gel directly calcined at 400 °C for 24 h without prior reaction in the autoclave.

The crystallite size was estimated from X-ray (d_{111}) line-broadening analysis using the Scherrers' equation [35].

$$D = \frac{0.9\lambda}{\beta \cos \theta'}$$

where D is the average particle size in nanometers, β is the half-width of the considered peak (in radians), λ is the wavelength of the X-ray (CuK α : 0.154 nm), and θ is the Bragg diffraction angle in degrees. The calculated values of the crystallite size for the PT samples, which were calcined at 450 °C for 10 h and 400 °C for 24 h, were 21.5 and 19 nm, respectively.

From the above descriptions, it is worth noting that the perovskite PT phase developed at a much lower temperature than those reported for most of other sol-gel routes. Generally, the homogeneous powders of smaller particle size undergo crystallization at lower temperatures [36]. The high calcination temperatures inevitably result in PT particle aggregation and coarsening, and therefore nonuniform morphology and mediocre electrical properties.

3.3. Proposed Particle Growth Mechanism

The synthesis of multicomponent oxide powders via chemical processes involves several metal-source chemicals and chelating ligands having different chemical reactivity. Thus, the powders with different morphologies and size have been reported when the chemicals that were involved in the synthesis procedures and the preparation techniques varied.

The faceted and equiaxed lead titanate powders are produced in wide range synthesis conditions regardless of the preparation route. In contrast, spherical perovskite materials can only be prepared under restricted and stringent situations. Therefore, it has been acknowledged that it is difficult to acquire spherical powders due to formation behavior. The non-spherical powders are not appropriate for certain categories of ceramic processing, such as sintering and forming [25]. Therefore, several methodologies have been attempted in order to develop oxide powders with spherical shape.

The “template formation” mechanism is based on the difference of the solubility of the reactants. The more soluble compound primary dissolves and then diffuses into the less soluble reactant through its surface and reacts in situ to form the desired phase. The morphology of grain composing the obtained phase retains that of the less soluble reactant, which plays the role of template. Cai et al. [28] played on the difference in the solubility of PbO and TiO₂ in NaCl-KCl to produce nearly spherical PbTiO₃ powders. PbO is soluble in the alkali chlorides, while TiO₂ does not dissolve. Thus, lead titanate formed at the TiO₂ grain surfaces. The prior synthesized spherical TiO₂ templates have been used to prepare various perovskite oxide powders of the same morphology. Spherical PbTiO₃, BaTiO₃, and SrTiO₃ have been produced by adding appropriate sources of A-site ions to TiO₂ templates [25].

In the present work, both lead and titanium precursors were completely dissolved in isopropanol by the assistance of acetoin as complexing ligand. Therefore, in our case, titanium oxide did not seem to function as a template to form lead titanate spherical particles. In our previous research work [37,38], we reported the effectiveness of several alkanolamines in preparing dense films and powders from alcoholic systems of metal alkoxides and acetates. These systems can also be extended to synthesize multicomponent materials since alkanolamine-alkoxide precursor solutions are very stable to hydrolysis.

In the present work several alkanolamine compounds such as monoethanolamine, diethanolamine, and triethanolamine have been tried to synthesize PT particles. However, only featureless powders could be prepared. In contrast, we found that spherical submicrometer particles can easily be prepared using acetoin as a complexing ligand. One possible reason for the formation of spherical powder is probably related to acetoin hindering the growth of crystal in specific directions, rendering all crystallographic directions equivalent. Acetoin may also have acted as a reagent after undergoing crotonic condensation, delivering water for the synthesis [39]. Another reason for using acetoin is that this ligand has a relatively low boiling temperature, and it is not as strong of a chelating agent as other alkanolamines that are often used in sol-gel processing. Therefore, we expect that the complex that forms will decompose at a lower temperature. This is quite important since the lead volatilization during calcination will be limited. Note that we have used stoichiometric composition in the precursor system (not excess lead to compensate for lead loss). Excess lead is known to segregate at the grain boundaries which deteriorate the ferroelectric properties of the material.

To understand the formation mechanism of the PT spherical particles, a schematic illustration of the particle growth is proposed as shown in Figure 11.

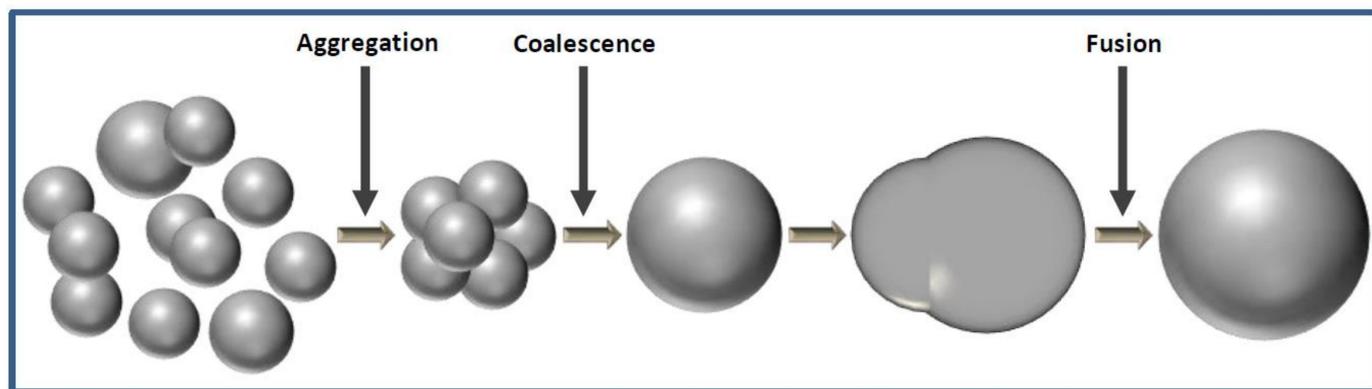


Figure 11. Schematic diagram of the formation of lead titanate spherical particles.

Primary spherical particles form during the period of nucleation. The formation of these spherical nanoparticles is a logical consequence of the sol-gel mechanism known as Micelle Templated Self Assembly of Ligands (MTSALs). In [40,41], the association of multiple primary particles forms aggregated particle clusters and spherical particulates

form via coalescence. In a later period, several particulates merge to form a definite particle (see inset of Figure 2b).

From the above discussion, it appears that:

- The use of acetoin as a ligand and the autoclave as the reaction medium are essential to form PT spherical particles.
- Nanometric primary PT particulates directly formed under autogenous pressure.
- The nanosized primary particulates weakly bond and confine within submicrometer spherical powders.

4. Summary

In this paper, a simple, straightforward, and one-step sol-gel approach was developed to synthesize perfectly spherical PT powders. In this study, the microscale PT particles with no aggregation were produced. The mean grain size of an isolated particle was about 4 μm . TEM micrographs confirmed the perfectly spherical shape of the PT powder particles and demonstrated that they were composed of many elementary nanometric crystals. Adjacent particles likely merge forming larger grains while keeping the general morphology. After calcination, the particles retained their spherical shape. The tetragonal nano-sized PT crystals were identified by X-ray analysis following calcination at 450 $^{\circ}\text{C}$ for 10 h. Several parameters were identified as important for controlling the shape of the particles, namely the thermal-treatment mode and the nature of the ligand.

Further investigation should be carried out to find out if the procedure developed in this study can be extended to prepare other perovskite compounds. We are currently studying the impact of the nanometric PT sub-particles on their ferroelectric and piezoelectric properties and sintering behavior.

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Conflicts of Interest: The authors declare no conflict of interest.

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