(3-hexylthiophene).[13,14] We postulated that the polymer photosensitizes singlet oxygen formation and that addition of the latter to thienyl rings is responsible for chain scission and disruption of the π-system. Precedence for this exists for monomeric thiophenes.[15,16]

The presence of oxygen is clearly a major factor in the solid-state photochemistry of P3HT and it appears that Diels-Alder addition of singlet oxygen to thienyl units occurs, as evidenced by the formation of a sulfine. This in itself would not lead to insolubilization of poly(3-hexylthiophene). The complete mechanism of photolysis probably involves photolysis of photolabile intermediates in order to achieve insolubilization. The full mechanism of photolysis is currently under investigation.

Conclusions

We have demonstrated a simple process for depositing fine π-conjugated polymeric patterns with controlled architecture. Upon oxidation the pattern is rendered electronically conducting. This technology has broad ramifications in the design of integrated circuitry and device fabrication. Possible applications include the formation of interconnects or channels of defined resistivity for microchips and printed circuitry, the deposition of π-conjugated nonlinear active waveguide components, and hybridization of organic and semiconductor components in chemical sensor manufacture.

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Preparation of Fine $PbTiO_3$ Powders by Hydrolysis of Alkoxide[†]

Jiming Ma,* Humin Cheng, Zhenguo Zhao, and Di Qiang

Department of Chemistry, Peking University
Beijing, China

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Introduction

During the past few years, many fine ceramic composites with different connectivity patterns have been designed and fabricated for making new materials in which desired properties can be incorporated through the use of a combination of materials with different properties. Among the composites, the 0-3 type has a better applicability because of its versatility in forming operation and the easiness in fabricating. Lead titanate (PT) with perovskite structure is a well-known ferroelectric material. Because of its high Curie temperature, low dielectric constant at low temperature, and high pyroelectric and large anisotropy coefficients, it is a very good material for high-frequency filters, IR detectors, and photoelectronic devices. The crux of achieving a 0-3 type of PT composite is the preparation of fine PT powders with desired particle size and size distribution. Conventional methods of making ceramic powders include thermal decomposition of inorganic salts, solid-solid reaction, coprecipatation in solution, and so on. Recently, the method using precursors of organometallic compounds, including alkoxides[1,2] and carboxylates,[3] has been used to produce a wide variety of ceramic materials in powder or monolithic form, because it can offer many advantages in producing ceramics, including high purity and homogeneity, low-temperature processing, and easy to form a variety of structures (macro and micro). The present work investigates the preparation of fine perovskite PT powders by hydrolysis of alkoxide and the influence of various factors on the particle size and structure of the resulting PT powders.

Table I. Effect of Alkoxide Concentration on the Particle Size of PT Powders

no.	wt ratio alkoxide/ isopropyl alcohol	$\bar{d}$, nm hydrolysate particle	$\bar{d}$, nm after calcination at 600 °C	wt % of particles with $d < 100$ nm
1	1:0	620	280	5.5
2	1:1	550	270	6.6
3	1:2	180	260	7.1
4	1:5	110	290	7.7
5	1:10	87[a]	250	10.4

[a] Determined by photocorrelation spectrometry.

Experimental Section

The Pb-Ti complex metal alkoxide was synthesized following the method described by Gurkovich and Blum,[2] except that tetrabutyl titanate and 2-ethoxyethanol were used instead of tetraisopropyl titanate and methoxyethanol. After removal of most of the 2-ethoxyethanol by distillation, the obtained complex alkoxide was diluted with solvent (e.g., isopropyl alcohol). The solution of complex alkoxide was added into a large amount of water under vigorous stirring, hydrolyzed to precipatate directly without an intermediate process of gelation. Therefore, this method is a modification of the sol-gel process.

The precipatates derived from the complex alkoxide were separated by filtration and dried at 80 °C for 48 h, and then the dried precipatates were calcinated in an oven using a heating rate of about 8 $°C\ min^{-1}$ to 600 °C and held at this temperature for about 2 h; fine light yellow $PbTiO_3$ powders were obtained.

The crystal structure was examined with a Rigaku D/max-ra X-ray diffractometer, IR absorption spectra were measured by a Nicolet 7199 B FTIR, Raman spectra were obtained by using a Spex 1407 Raman spectrometer, the DTA and TG analyses were determined by a LCT-1 type of differential thermal analyzer.

A Horiba-CAPA 500 centrifugal particle size analyzer was used to measure the weight-average particle size and size distribution of lead titanate powders dispersed in water. TEM observations were also made by using a JEM-200 CX type TEM.

The XRD pattern of the PT powders prepared according to the aforementioned method is completely consistent with that of perovskite $PbTiO_3$, and the ratio of Pb/Ti is 1.003, determined by using a Jarrell-Ash ICAP-9000 plasma spectrometer, indicating that the product is pure perovskite $PbTiO_3$. The ratio of c/a is determined to be 1.065, consistent with the theoretical value of tetragonal $PbTiO_3$.

Results and Discussion

Effect of Hydrolysis Conditions on the Particle Size of PT Powders. The effects of various hydrolysis conditions, such as manner of hydrolysis and amount of water, solvent and concentration of the complex alkoxide, temperature, pH and the addition of dispersant, etc., on the particle size of resulting PT powders have been examined. The results demonstrate that the above factors may have an apparent effect on the size of hydrolysate particles, but none of them exhibits a regular influence on

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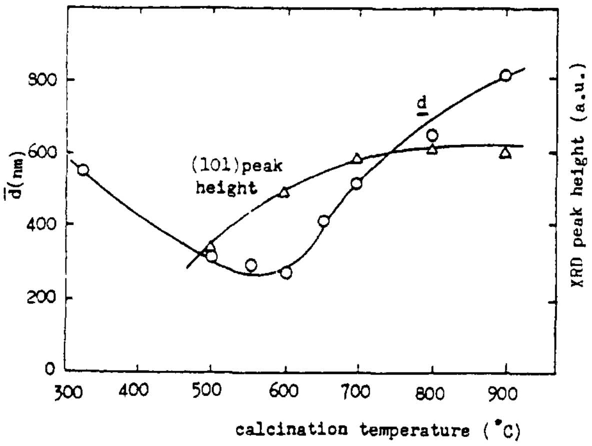

Figure 1. Effect of calcination temperature on the particle size of PT powders.

the particle size of the calcinated PT powders. For instance, a series of complex alkoxide solutions in isopropyl alcohol with different concentrations were prepared by diluting the complex alkoxide with various amounts of isopropyl alcohol and then hydrolyzed to form precipitates. The particle size of the hydrolysate was determined before the separation of hydrolysate from solution and after calcination at 600 °C for 2 h. The results (Table I) show that the more dilute the alkoxide solutions are, the finer of the hydrolysate particles. However, the average particle size of the PT powders after calcination at 600 °C appear to be independent from the concentration of the alkoxide solutions, although the lower concentration of alkoxide solution seems to be favorable to the formation of finer particle (<100 nm) of PT powders.

Effect of Calcination Conditions on the Particle Size of PT Powders. (1) Calcination Temperature. The results of XRD indicate that the $PbTiO_3$ crystals with perovskite structure begin to form at about 440 °C, essentially consistent with the results obtained by Gurkovich and Blum.[9] To examine the effect of calcination temperature on the particle size of PT powders, the hydrolysate of complex alkoxide was heated to different temperature at 8 °C/min, and the total heating time was maintained at 3 h. The particle size of the resulting PT powders was determined by usng a Horiba-CAPA 500 particle size analyzer, and the results are shown in Figure 1. The particle size of dried hydrolysate, being about 560 nm before calcination, was found to decrease initially with the increasing temperature, reach a minimum of about 260 nm at ca. 600 °C, followed by a rapid increase of the particle size with the increasing temperature.

The appearance of a minimum in the particle size–calcination temperature curve may be explained as follows. The hydrolysate of complex alkoxide is amorphous before calcination and the particles may form an agglomerate in water, which is used as the medium for determining the particle size, by the residual organics or organical groups on the particle surface, showing a large particle size. As the calcination temperature increases, the degree of crystallization of the PT powders, as shown by the (101) peak height in Figure 1, and accordingly the grain size demonstrates a substantial increase. At higher temperature, sintering of particles may occur. On the other hand, the above factors causing the agglomeration of particles, such as the residual organics or organical groups on the particle surface, would be diminished to a greater extent at higher calcination temperation, and hence decrease the degree of agglomeration. The combination of the above two contrary factors may result in a minimum of particle size at about 600 °C. The TEM observation on the PT powders obtained at different temperatures is qualitatively consistent with the above assumption.

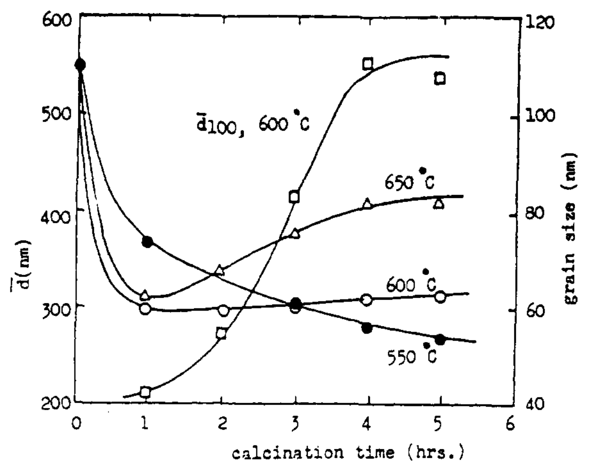

Figure 2. Effect of calcination time on the particle size of PT powders.

(2) Calcination Time. The hydrolysate of alkoxide was calcinated for different hold time at 550, 600, and 650 °C, respectively, and the particle size of the resulting PT powders was shown in Figure 2. As can be seen from Figure 2, the pattern of the varying particle size of PT powders as a function of calcination time at the three different temperatures are different from each other. After the rapid decrease of particle size after the initial hour, the particle size of PT powders calcinated at 550 °C continuously decreases, that of PT powders calcinated at 600 °C keeps essentially unchanged, and the sample calcinated at 650 °C increases. The grain size (600 °C, D_{100}) was determined to be continuously growing with increasing calcination time. Apparently, while the grain size will increase as the heating time prolongs, the agglomeration between particles will be weakened to some extent. At relatively higher temperature, the later process may complete quite rapidly, thereafter the growing and sintering of grains become predominant. At lower temperature, the growing and sintering of grains slow down, the weakening of agglomeration between particles may become the predominant factor, and hence the particle size shows a steady decrease over 5 h.

(3) Mechanism of Formation of $PbTiO_3$ by Hydrolysis of Alkoxide. The reaction between tetra-*n*-butyl titanate and lead acetate can be expressed by the following equation:[4-6]

$$Ti(O\text{-}t\text{-}Bu)_4 + Pb(CH_3COO)_2 \rightarrow PbTiO_2(O\text{-}t\text{-}Bu)_2 + 2CH_3COO\text{-}t\text{-}Bu$$

After hydrolysis of the resulting complex alkoxide and heat treatment, the lead titanate with perovskite structure was obtained. As for the composition of the hydrolysate, it is still an open question in the literature.[7,8] It is noted from the DTA curve (Figure 3) that there are two exothermic peaks at about 250 and 460 °C, respectively, during the conversion process from hydrolysate to final product. The corresponding XRD results (Figure 4) ob-

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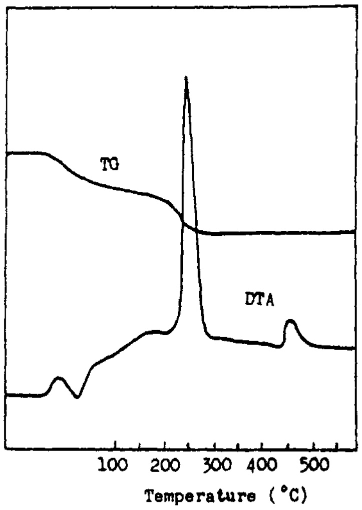

Figure 3. DTA and TG analysis of hydrolysate of complex alkoxide.

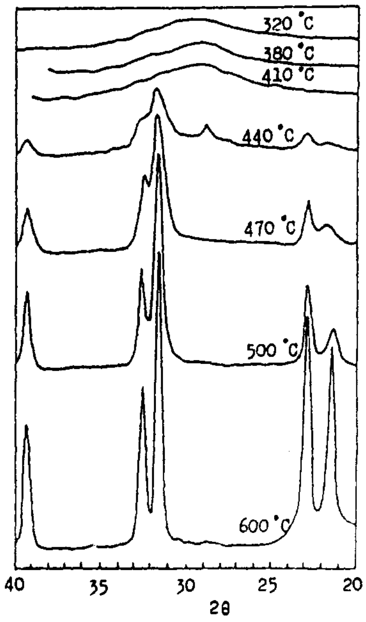

Figure 4. XRD patterns of PT powders calcinated at different temperatures.

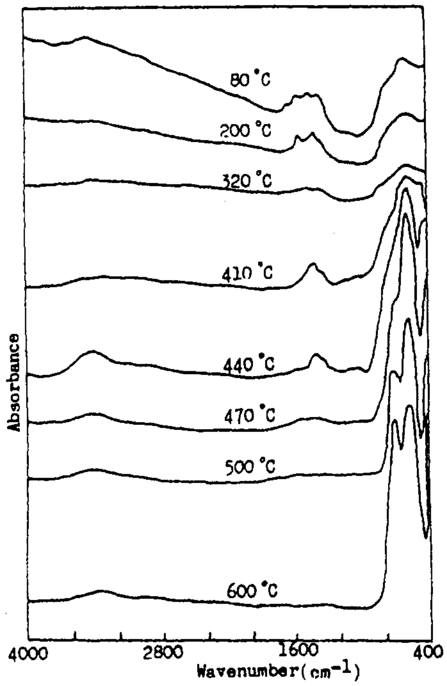

Figure 5. IR pattern of PT powders calcinated at different temperatures.

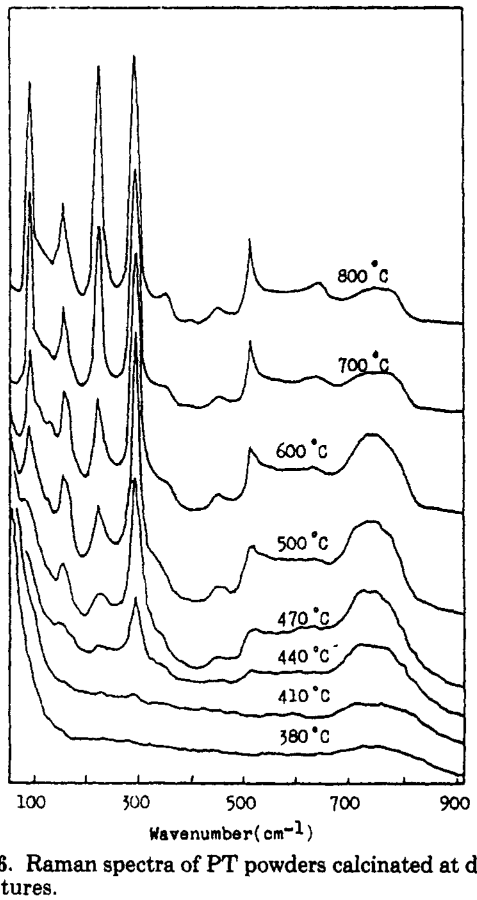

Figure 6. Raman spectra of PT powders calcinated at different temperatures.

tained on samples calcinated at different temperature for 3 h show an amorphous pattern at a temperature lower than 410 °C, and the characteristic peaks corresponding to tetragonal $PbTiO_3$ appear at 440 °C, implying that the exothermic peak at about 460 °C on the DTA curve corresponds to the formation of perovskite phase of $PbTiO_3$. Since no weight loss was observed in this temperature range, the appearance of perovskite phase of $PbTiO_3$ only can be a result of either the conversion from amorphous to perovskite phase or the reaction between PbO and TiO_2. Gurkovich and Blum[9] believed that the former process was responsible. However, the IR results (Figure 5) demonstrate that the characteristic peaks of $PbTiO_3$ (~570 and 710 cm^{-1} at the range 400–800 cm^{-1}) were not observed until 440 °C; this tendency is shown more pronouncedly on the Raman spectra obtained by using a Spex 1407 Raman spectrometer (Figure 6). It is unlikely that the substantial dissimilarity between the samples calcinated above and below 440 °C is due to the difference of the crystallinity. We conjecture that the formation of $PbTiO_3$ and the crystallization probably to be completed simultaneously around 460 °C; before then the sample is likely to be a homogeneous mixture of PbO and TiO_2 instead of amorphous $PbTiO_3$. The IR and Raman spectra did not demonstrate direct evidence for the existence of PbO and TiO_2; one of the reasons may be the location of the characteristic peaks of the oxides. For instance, the characteristic peak of IR spectrum of TiO_2 is at about 370 cm^{-1}, which is out of the wavenumber range of the instrument we used, and hence whether or not TiO_2 exists cannot be concluded with certainty from IR spectrum. To further interpret the mechanism of forming $PbTiO_3$ by hydrolysis of alkoxide, the hydrolysate which had been calcinated for 3 h at 400 °C was treated with 1:1 acetic acid; after filtration dilute H_2SO_4 was added into the filtrate, and a large amount of white precipitate was observed. The precipitate was confirmed to be $PbSO_4$ by XRD analysis, indicating that the sample contains free PbO in large amount. Meanwhile, the sample calcinated at 600 °C exhibited only slight turbidity at the same condition, probably due to a small amount of excess PbO, and the sample calcinated at 800 °C showed no precipitate at all. These results indicate that although a complex alkoxide of lead and titanium was formed in the reaction,[7,8] it may be converted to hydrolysates of Pb and Ti alkoxides individually during hydrolysis and then to a mixture of their respective hydrous oxides with a high degree of homogeneous mixing. The formation of hydrous oxides seems to be an inevitable intermediate step in the conversion process from hydrolysate of alkoxide to perovskite phase of $PbTiO_3$ by calcination.

Molecular Recognition in Microporous Organo-Minerals. Shape-Specific Interactions of Carbon Dioxide in Functionalized Organo-Montmorillonite Microcavities

Hongbai Lao, Sylvie Latieule, and
Christian Detellier*

Ottawa-Carleton Chemistry Institute
University of Ottawa Campus
Ottawa, Ontario, Canada K1N 6N5

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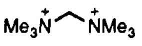
The study of the microporosity of organo-smectites was pioneered in the 1950s by Barrer.[1] In a series of papers,[1] which he recently reviewed,[2] Barrer, with his co-workers, showed that when the natural interlamellar inorganic cations of montmorillonite and hectorite are replaced by small alkylammonium organic cations, permanent microporosity is created, and sorption of gases and of organic molecules is very favored.

Polymeric,[3] ceramic,[4] or composite[5] membranes have been developed for gas-separation purposes, including the separation of gaseous mixtures of CO_2 and CH_4. Ion-exchange modified zeolites were used for chromatographic gas separation.[6]

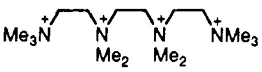
The incorporation of organic cations into smectites can result in a microporous material with a network of cavities whose height and volume are controlled by the size and the shape of the organic cation. Moreover, functionalities, such as ester groups, can be attached to the organic cation, so that one can easily synthesize a material with tortuous channels whose walls combine hexagonal arrays of silicate oxygens and organic functions. Given the almost infinite availability of potential organic intercalates, a large flexibility is offered in the design of these materials, which could be tailored for specific recognition and separation purposes.

The gas chromatographic properties of such organo-smectites are reported in this paper, with a focus on their ability in separating carbon dioxide–methane mixtures. The shape of the microcavities is the most important parameter controlling the gas interactions with the microcavities walls.

The clay material was a source clay, SWy-1, obtained from the Clay Source Repository, University of Missouri. The <0.2-μm fraction was obtained according to standard gravitation procedures.[7] It was checked by particle size analysis (Sedigraph 5100) that more than 90% of the sample was <0.2 μm esd. The homoionic Na^+ montmorillonite (Na-M) was prepared, purified by dialysis, and freeze-dried. Ten different quaternarized and esterified amino acid derivatives were prepared[8] and incorporated into the interlamellar spaces of Na-M, at full cationic exchange capacity (cec; 87 ± 5 mequiv/100 g of Na-M). The percentage of incorporation was controlled by determination both of the quantity of sodium released (sodium selective electrode) and of the quantity of organic cation absorbed (colorimetric methods). In all the cases, the amine function of the amino acid was trimethylated. Both amine functions were trimethylated in the cases of Orn and Lys.[9] Tetramethylammonium and some quaternarized polyammonium cations (**1**–**3**)[10] were also incorporated at full loading of the clay (100% of the cec). The organo-clay was dried under vacuum at 60 °C overnight. Particles of size 60–120 mesh were selected as packing material for chromatographic columns (3 ft × 1/8 in. o.d.). Prior to use, the packed column was conditioned under He flow at 90 °C for 8 h. It was checked that the results could be reproduced with columns aged more than 2 months and reconditioned prior to use:


1 (MMDA)


2 (MEDA)


3 (MTETA)

The interlamellar distances (i.d. = d_{001} − 9.6 Å)[11] of the organo-clays were systematically measured and found to be in the range 4.0–5.0 Å, showing that the trimethylammonium group (height measured on space-filling models, 5.0 Å) determines the interlamellar distance, with the side chains of the organic derivatives lying parallel to the clay surfaces.

Figure 1 shows typical chromatograms. While no separation was observed for Na-M (i.d. = 2.8 Å), CO_2/CH_4 separation factors of 12 and 20 were obtained for ORN-Me-M and MTETA-M, respectively. The retention times and the separation factors (ratios of retention times of CO_2 and CH_4 relative to air)[12] were highly dependent upon the

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