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습식화학법으로 제조된 티탄산 납의 형상

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Morphology of Lead Titanate Prepared by Wet Chemical Methods

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요 약

졸겔 및 공침법으로 제조된 티탄산 납 분말의 형태를 하소온도와 하소시간의 함수로 조사하였다. 질산 납과 사염화 티탄의 혼합용액을 사용하여 40−43℃ 및 9.0−9.7 pH에서 $PbTiO_3$ 전구체를 제조하였으며, 350−1000℃에서 1−10시간동안 공기중에서 이들을 하소시켰다. 하소온도와 시간의 증가에 따라 입자의 크기가 증가하고 응집이 심화되었다. 졸겔법으로 제조된 분말을 700℃에서 하소시킬 때, 초기에 형성된 침상형 혹은 각주형의 입자들은 하소가 진행됨에 따라 다면체형으로 변한뒤, 모서리가 둥근 다면체형 입자로 성장하였다. 공침법으로 제조된 분말은 결정화 과정중에 형태가 변화되지 않았다.

Abstract

The morphology of lead titanate powders prepared by sol-gel and coprecipitation techniques was investigated as a function of firing temperature and soaking time. $PbTiO_3$ precursor powders were derived from a mixed solution of lead nitrate and titanium tetrachloride at 40℃ to 43℃ and pH of 9.0 to 9.7, and fired at temperatures 350−1000 ℃ for 1−10 h in air. An increase of particle size and agglomeration with increasing calcination temperature and duration could be observed. By annealing sol-gel derived powder at 700℃, the initially-formed acicular(and/or prismatic) primary particles transformed to polyhedral shape with soaking time, and further soaking caused coarsening the polyhedral particles with rounded edges. However, the morphology of the coprecipitated powders was not varied during crystallization

Ⅰ. INTRODUCTION

Potential advantages of wet-chemically derived ceramic powders, especially prepared by the sol-gel and coprecipitation methods, over conventional powders are controllable size and shape, molecular scale homogeneity, and the enhancement of reactivity. However, because of the very fine and irregularly shaped particles which are often found in the powders, problems in firing and sintering are often encountered. Much of the work has been done with multicomponent oxides such as $PbZrO_3$, $Pb(Zr,Ti)O_3$, $PbTiO_3$.[1-3]

Pure $PbTiO_3$ can be prepared in the amorphous state by coprecipitation and sol-gel techniques, and a controlled crystallization of the amorphous $PbTiO_3$ can be accomplished by heating from 450 ℃ to 600℃.[3-9] The crystallization process has been investigated by using DTA, Raman spectroscopy, and dielectric properties. Crystallization temperature is indicated by an exothermic peak in the DTA curve during heating. Beginning with the sol-gel derived amorphous $PbTiO_3$, crystallization has been observed to begin upon annealing at 400℃ for approximately 6 h.[3] Raman spectra of the coprecipitated and sol-gel derived amorphous $PbTiO_3$ heat-treated above crystallization temperature up to 700℃, show that the crystallization yields a mixture of amorphous and cyrstalline phases.[9] With increasing calcination temperature and time, the as-prepared coprecipitated powders of equidimensional particles approximately 10 nm in size sinter and grow to form equidimensional crystalline particles between 20 and 100 nm primarily with cubic or distorted tetragonal symmetry, which grow in size(50−200nm) and transform to the tetragonal state(up to 400 nm).[10,11]

In this study, coprecipitated and sol-gel derived $PbTiO_3$ were prepared from $Pb(NO_3)_2$ and $TiCl_4$, and the morphology of $PbTiO_3$ powders was investigated as a function of firing temperature and soaking time. Phase transformation temperatures were determined from DTA and TGA results. Morphology and particle size of the resulting products were analyzed by using TEM and BET surface area analyzer.

Ⅱ. EXPERIMENTAL PROEDURE

The $PbTiO_3$ preparation procedure by a sol-gel process from an aqueous solution of lead nitrate and titanium tetrachloride has been described in author's previous works.[2,4] A weighed quantity of $Pb(NO_3)_2$* was dissolved in deionized water and the titanyl solution was prepared by slowly adding $TiCl_4$** to chilled water. To prepare $PbTiO_3$ sol, the aqueous solutions were mixed in the presence of NH_4NO_3, and the $PbTiO_3$ gel was prepared at 40℃ to 43℃ and a pH of 9.0. The pH was controlled by adding NH_4OH. This gel was dehydrated at 60℃ to 70℃ for 72 h in a vacuum. The coprecipitated powder was derived from the mixed aqueous solution, which was stabilized by adding 1.1 mol of H_2O_2 to 1 mol of $PbTiO_3$. The clear mixed solution was added into a continuously agitated bath of NH_4OH and water, where the temperature of the reactor bath remained constant 40℃ to 43℃ and the pH of the solution was adjusted to 9.6 to 9.7. The precipitates were filtered, rinsed, and dried at 80℃ to 100℃. The precipitates and gels were calcined at 350−1000℃ for 0.5−10 h in air.

In order to compare $PbTiO_3$ powders prepared by wet chemical methods to those prepared by a solid state reaction, $PbTiO_3$ powder was also synthesized from PbO and TiO_2 powders as follows; The raw materials used were PbO*** and TiO_2**** powders. Powders were weighed in the proportion so that the molar ratio $PbO/TiO_2=1.0$, wet-ball milled for 12 h, dried at 80-100℃ for 12 h, and then calcined at 800℃ for 1 h in a covered platinum crucible. The calcined powders were

ground again by wet-ball milling for 8 h, and then dried at 80-100℃ for 12 h.

The transformation temperatures and the weight losses were monitored by DTA and TGA[+]. Thermal runs were carried out for the dried gels and the sample was heated at a constant rate of 5 ℃/min. The crystalline phases which appeared during the thermal treatments were analyzed by means of x-ray diffraction(XRD). XRD patterns were taken by a x-ray diffractometer[++] using CuK α radiation. In order to investigate morphology and particle size of the calcined powders, powders were dispersed in iso-propyl alcohol with an ultrasonic vibrator for 12 h. Electron micrographs of the dispersed powders were taken by transmission electron microscope(TEM)[+++]. Surface areas of powders were measured from BET surface area analyzer[++++]

Ⅲ. RESELTS AND DISCUSSION

Electron micrographs of the dried gel and the gels calcined at 400-700℃ are shown in Fig.1. Gels calcined at 400℃ are amorphous in XRD patterns, while crystalline $PbTiO_3$ is formed by calcining the gel at temperature higher than 500℃. The dried gel and the gel calcined at 350-400℃ show a uniform network, where the particles are coarsened at 400℃. As calcined at 500℃ and 600℃, powders are comprised of acicular particles with a few prismatic particles, where the fraction of prismatic particles in the powder calcined at 600℃ is higher than that in the powder calcined at 500℃. Powders calcined at 700℃ consist of primarily prismatic particles with a few acicular and polyhedral also, but at 800-1000℃ the morphology of the particles could not be delineated clearly due to agglomeration of the particles.

The effect of firing time on the morphology of $PbTiO_3$ powders calcined at 700℃ is shown in Fig. 2. At the initial stage of reaction(soaking for 1 h), the acicular, prismatic and polyhedral particles are observed. Upon further heating(for 2-5 h), the number of very long acicular particles with large aspect ratio(c/a) decreases, while that of small prismatic and polyhedral particles increases. Also the edges of prismatic particles become rounded in order to decrease the surface energy. Soaking for 10 h, the prismatic powders are seldom observed and the coarsened polyhedral particles with rounded edges predominate. Fig.3 shows the variation of the BET specific surface area with firing time at 700℃, which is in good agreement with the morphological changes with soaking time as shown in Fig.2. During the initial stage of 0.5-1 h, the growth of acicular, prismatic, and polyhedral particles reduces the total surface area of the powders. For longer soaking time(1-3 h), the number of acicular and prismatic particles diminishes, whereas the number of small polyhedral particles increases. Upon this, the specific surface area increases with soaking time. And yet, the mechanism and process for the disappearance of acicular and prismatic particles and/or the creation of new polyhedral particles are not known. Upon further heating, all

*) ACS reagent, Alfa, Danvers, MA, USA.

**) 99.9% purity, Alfa.

***) J. T. Baker, purity 99.5%, average particle size of 1.0μm.

****) J. T. Baker, purity 99.5%, average particle size of 0.45μm.

[+]) Dupont 990 DSC equipment, E. I. Du Pont Co., Wilmington, DE, USA.

[++]) Rigaku D/max-IIIA, Rigaku Denki Co., Japan.

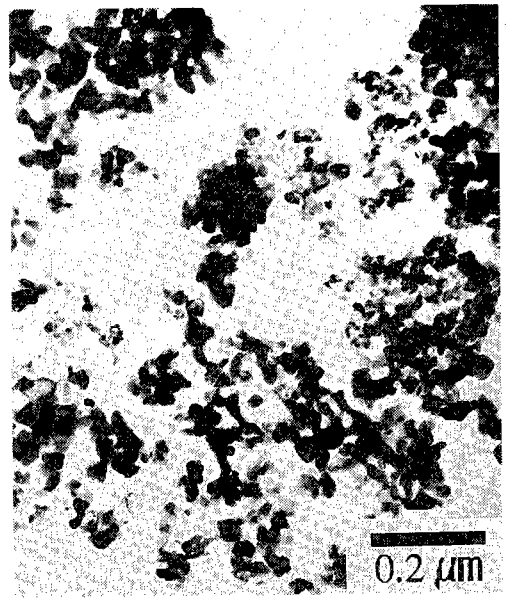
[+++]) Hitachi H-600, Hitachi Electric Co., Japan.

[++++]) Micromeritics 2100E, Accusorb 2100E.

the particles grow, and the surface area decreases again with time.

Electron micrographs of the coprecipitated $PbTiO_3$ powders calcined at 400-700℃ are shown in Fig.4. In the initial stage of annealing(0.5-1 h) at 400℃, the peaks of XRD patterns are very broad and the morphology of the particles is not well defined. After 24 h of annealing at 400℃, we

(a)



(b)

(c)

(d)

Fig.1. Transmission electron micrographs of(a) as-dried gel and of the resulting gels calcined for 1 h in air at (b) 400℃, (c) 500℃, and (d) 700℃.

can see well defined crystallites but agglomerated, where powders are poorly crystallized. The particle size is about 20-30 nm with round edges, which is in agreement with the results of XRD and BET

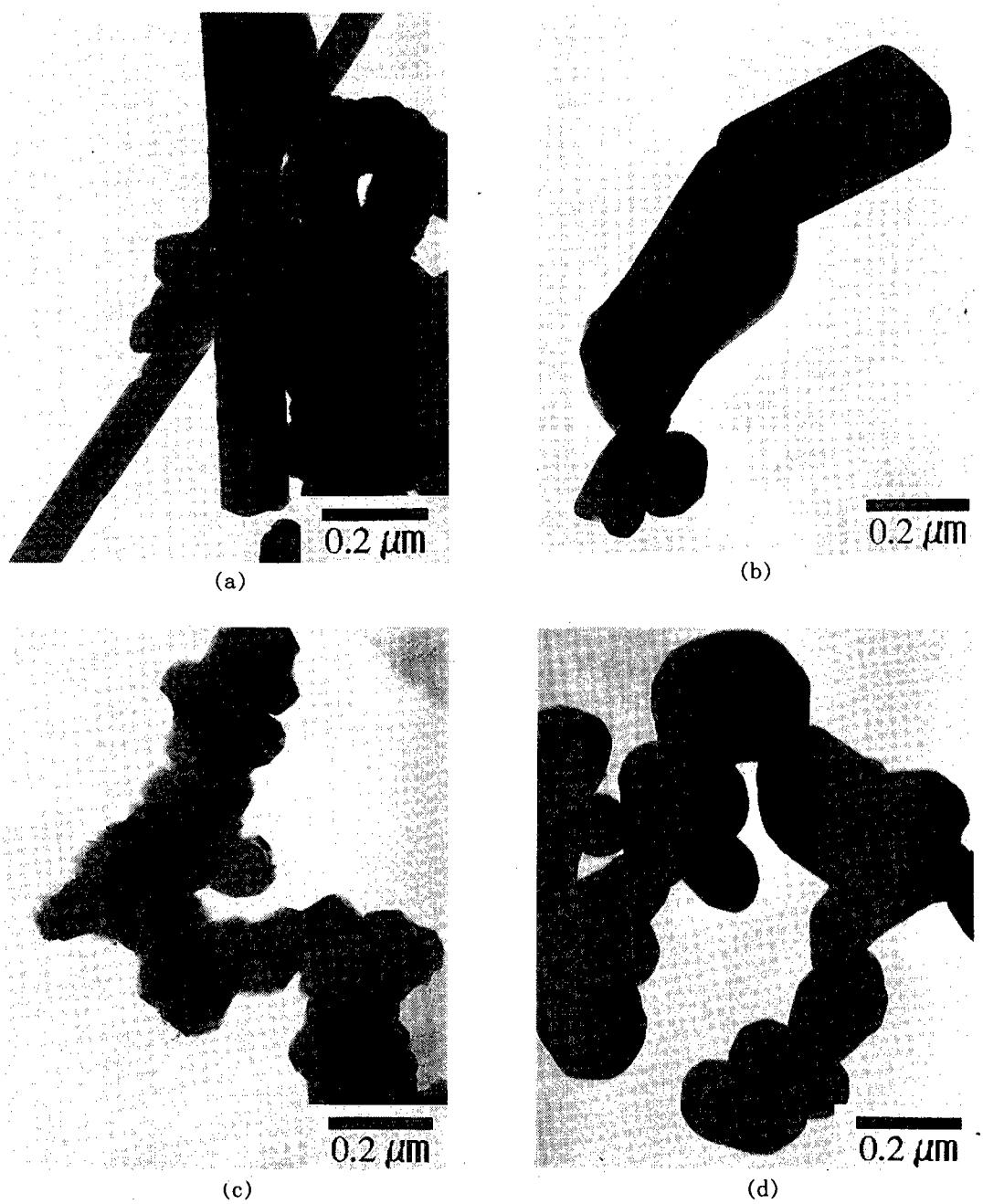


Fig.2. Transmission electron micrographs of sol-gel derived $PbTiO_3$ powders, calcined at 700 ℃ for (a) 1h, (b) 4h, (c) 4h, and (d) 10h.

surface area analysis. An increase of particle size with calcination temperature can be seen in the figure. For the powder calcined at 500℃, some fringes could be seen probably due to the superposition of very thin particles or defects(i.e. twinning, stacking fault etc.). However, these fringes are not seen in powders calcined at 400℃. As calcining at 700℃, powders are of well-developed crystalline $PbTiO_3$ with polyhedral shape. Faceted crystalline particles of 150-300nm in diameter are surrounded by clusters of small amorphous particles,[11] which agrees well with our previous result on Raman spectral change during crystallization, which is shown in reference 9. During calcining the coprecipitated powders, the morphological changes could not be found in the annealing temperature range of 400℃ to 700℃.

The evolving particle morphology and stability in wet chemical process is affected by condensation process, anion, catalyst, and chemical modification.[12] Two partially hydrolyzed molecules can link together in a condensation reaction. One kind of condensation is directed preferentially toward the ends of chains, resulting in more extended, less highly branched polymers. And the other is directed toward the middles of chains, leading to more compact, highly branched species. By annealing the coprecipitated lead-titanate amorphous powder relaxes to the gel structure at a temperature of about 350℃ and then transforms to crystalline $PbTiO_3$ powder at 500℃.[9] The dried gel is less dense than the annealed coprecipitated powder. Considering the discrepancy of morphological changes between the sol-gel derived and coprecipitated powder during cyrstallization, it could be assumed that the structure of the dried gel, a polymer network, is different from that of the coprecipitated powder with gel structure, which is annealed at 350℃. It is also assumed that the dried gel is less highly branched polymer, whereas the annealed coprecipitated powder is of highly crosslinked polymer because of its dense structure.

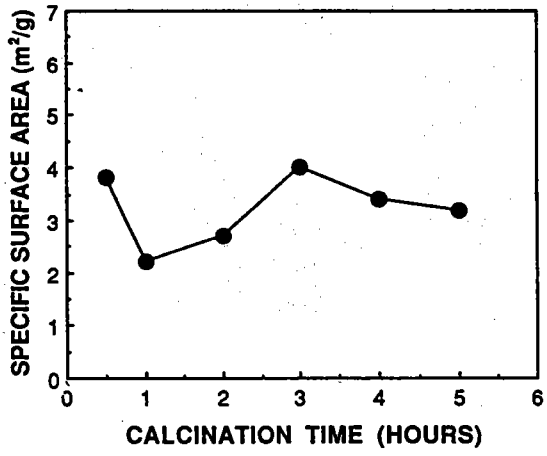


Fig.3 Variation of specific surface area with soaking time of 0.5－5 h, fired at 700℃ in air.

Particle shapes of $PbTiO_3$ powders prepared by a solid state reaction at 800℃ are shown in Fig. 5. Room temperature x-ray diffraction pattern shows that the calcined powder has crystallized to $PbTiO_3$ (tetragonal; a=0.392nm, c=0.417nm). The crystal symmetry and lattice parameters are similar to those of powders prepared by wet chemical methods. The sol-gel derived $PbTiO_3$ powders are composed of prismatic and polyhedral particles with rounded edges. Although the particle morphology shown in Fig.5 is similar to that in Fig.4(d), the average size of particles prepared by a solid state reaction is bigger than that prepared by wet chemical methods(at least quadruple), which are analyzed from the results of BET surface area analysis. Therefore, more fine particles are obtained from sol-gel process.

Ⅳ. CONCLUSION

During crystallization, the morphological change of the sol-gel derived $PbTiO_3$ powders was complex. By annealing sol-gel derived powder at 700℃, the initially-formed acicular(and/or pris-

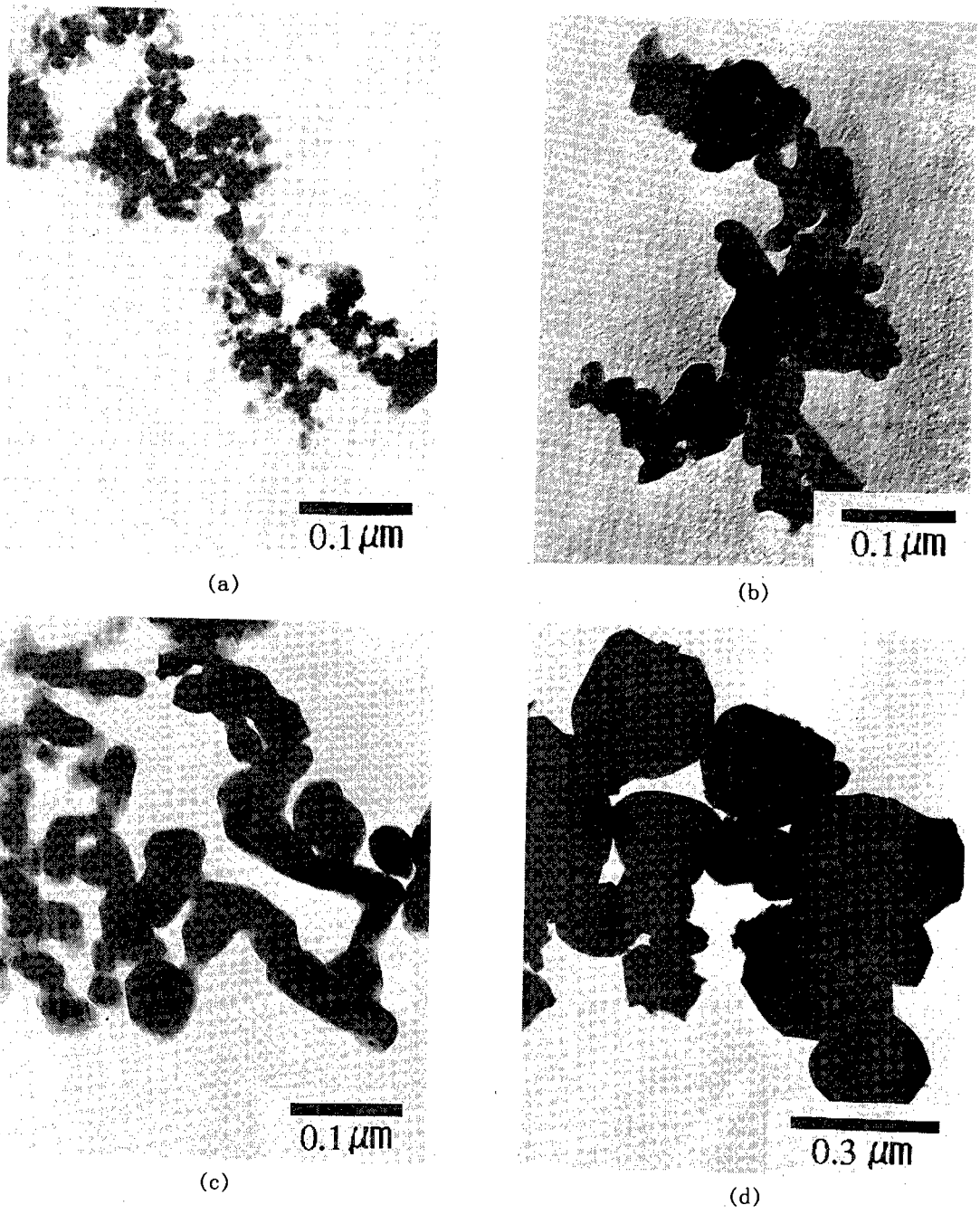


Fig.4. Transmission electron microgrphs of coprecipitated $PbTiO_3$ powders, calcined at 400℃ for (a) 1 h and (b) 24 h, (c) at 500℃ for 1 h, and (d) at 700℃ for 1 h.

matic) primary particles transformed to polyhedral shape with soaking time, and further soaking caused coarsening the polyhedral particles with rounded edges. However, the morphology of the

coprecipitated powders was not varied during cyrstallization. Considering the discrepancy of morphological changes during crystallization, it could be assumed that the structure of the dried gel, a less highly branched polymer network, is different from that of the coprecipitated powder with gel structure, which is annealed at 350℃. More detail works are needed to understand the morphological change, the crystallization process, the structure of gel and coprecipitate, and the structural relaxation during heating

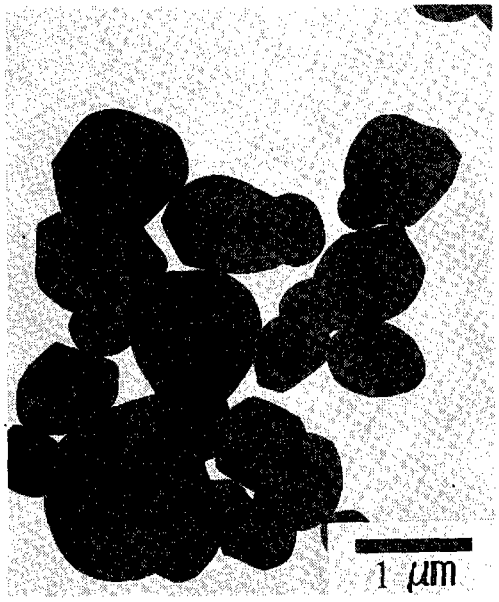


Fig.5. Transmission electron micrographs of $PbTiO_3$ powder, prepared by a solid state reaction, calcined at 800℃ for 1 h in air.

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