

Crystallization of $PbTiO_3$ Prepared by Wet-Chemical Methods

Byung-Cheul Choi and Moon-Ho Lee

Department of Metallurgical Engineering, Yeungnam University

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습식 화학법으로 제조된 $PbTiO_3$ 의 결정화

최병철 · 이문호

영남대학교 금속공학과

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ABSTRACT

The crystallization behavior of lead titanate powders prepared by sol-gel and coprecipitation techniques was investigated. The lead titanate precursors were derived from a mixed solution of lead nitrate and titanium tetrachloride at 40°C to 43°C and pH of 9.00 to 9.75. The X-ray diffraction patterns of the dried gel and coprecipitated powders showed it to be amorphous. DTA runs of the powders indicated crystallization to occur at 475~480°C. However, the amorphous powders were partially crystallized at 400~450°C with sufficient annealing time. The room temperature Raman spectra from heat-treated powders changed continuously from amorphous to crystalline state with increasing heat-treating temperature. By annealing coprecipitated powders, a dramatic change in the Raman spectra due to the structural relaxation as the annealing temperatures increased, was clearly visible, i.e., coprecipitated, gel, and crystalline structure, in turn.

요 약

졸겔 및 공침법으로 제조된 $PbTiO_3$ 분말의 결정화 거동을 조사하였다. 40~43°C 및 pH=9.00~9.75의 반응조건에서 질산염과 사염화 티타늄의 혼합용액으로부터 $PbTiO_3$ 전구체를 제조하였다. X-선 회절실험 결과, 건조된 겔과 공침분말은 비정질 구조를 나타내었다. 시차열분석(DTA) 시험을 행한 결과, 이들은 475~480°C에서 결정화되기 시작하였으나, 400~450°C에서도 충분한 시간동안 소둔시킬 경우에는 부분적으로 결정화되었다. 열처리된 분말에 대해서 상온 Raman 스펙트럼 분석을 행한 결과, 열처리온도가 증가함에 따라 비정질에서 결정상으로 스펙트럼이 연속적으로 변화되었으며, 공침물 구조는 겔구조로 변화된 후에 최종적으로 결정상 구조로 구조완화가 일어나는 것을 알 수 있었다.

1. Introduction

The work on chemical preparation of ceramic oxides, especially for electronic applications, has increased significantly in recent years. The sol-gel and coprecipitation methods, which utilize solution chemistry, offer advantages over traditional processing techniques because of higher purity, better homogeneity, lower processing temperatures, and improved material properties. Pure $PbTiO_3$ can be prepared in the amorphous state by sol-gel or coprecipitation techniques. A controlled crystallization of the amorphous $PbTiO_3$ can be accom-

plished by heating from 450°C to 600°C¹⁻³. The crystallization process has been investigated by using DTA, Raman spectroscopy, and dielectric properties¹⁻⁷. Crystallization temperature is indicated by exothermic peak in the DTA curve during isochronal heating. The amorphous $PbTiO_3$ prepared by wet-chemical method is not in equilibrium but is relaxing toward a stable crystalline state. Over sufficient annealing time, it has the possibility of transformation into the crystalline state even by isothermal heating at a temperature, well below the crystallization temperature³. In the previous work², the effects of pH and temperature for sol-gel

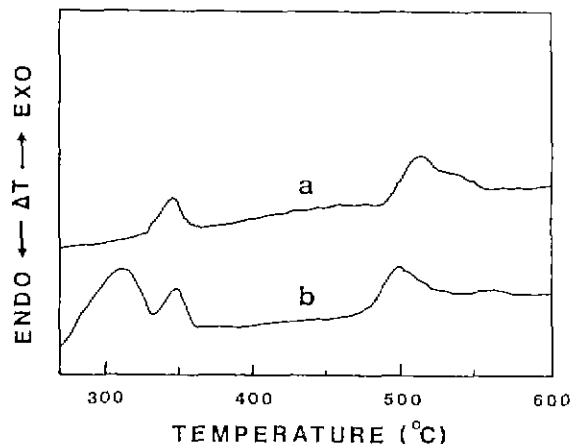


Fig. 1. Typical DTA curves for (a) coprecipitated PbTiO_3 powders and (b) dried PbTiO_3 gel.

processing within the PbO-TiO_2 system were investigated by using raw materials such as lead nitrate and titanium tetrachloride. In this study, lead titanate was prepared from lead nitrate and titanium tetrachloride. Phase transformation temperature was determined from DTA results. The crystallization processes and the structural relaxation of PbTiO_3 from the amorphous state were investigated by X-ray diffraction (XRD) patterns and Raman spectra. Changes in crystallization as a function of annealing time during isothermal heating at 400~450°C were also investigated.

2. Experimental

PbTiO_3 powders were prepared from an aqueous solution of reactants mixed in one molar stoichiometric ratio. The raw materials used were lead nitrate* and titanium tetrachloride⁺. A weighed quantity of lead nitrate 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 ammonium nitrate, and PbTiO_3 gels were prepared from the mixed solution at 40~43°C and 9.0 pH. The pH was controlled by adding ammonium hydroxide. This gel was dehydrated at 60~70°C for 72 hr in vacuum. The coprecipitated powders were derived from the mixed aqueous solution, which was stabilized by adding 1.1 moles of hy-

*ACS reagent, Alfa, Danvers, MA, U.S.A.

⁺99.9% purity, Alfa.

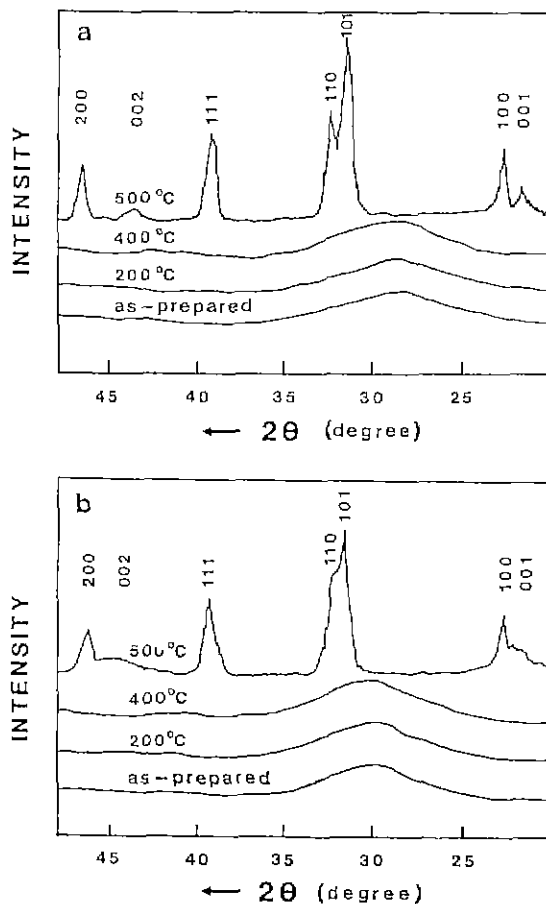


Fig. 2. X-ray diffraction patterns of (a) coprecipitated PbTiO_3 and (b) sol-gel derived PbTiO_3 , calcined for 30 min at 200~500°C.

drogen peroxide to 1 mole PbTiO_3 . The temperature of the reactor was remained constant at 40~43°C and the pH of the solution was adjusted to 9.60~9.75 by adding ammonium hydroxide. The precipitates were filtered, rinsed, and dried at 80~100°C. The transformation temperatures were determined by DTA runs carried out on dried precipitates at a constant heating rate of 10°C/min. The powders were calcined at 200~800°C for 10 min to 24 hr. The crystalline phase in the annealed powders was identified from XRD patterns and Raman spectra.

3. Results and Discussion

Figs. 1 and 2 show the traces of the DTA runs and

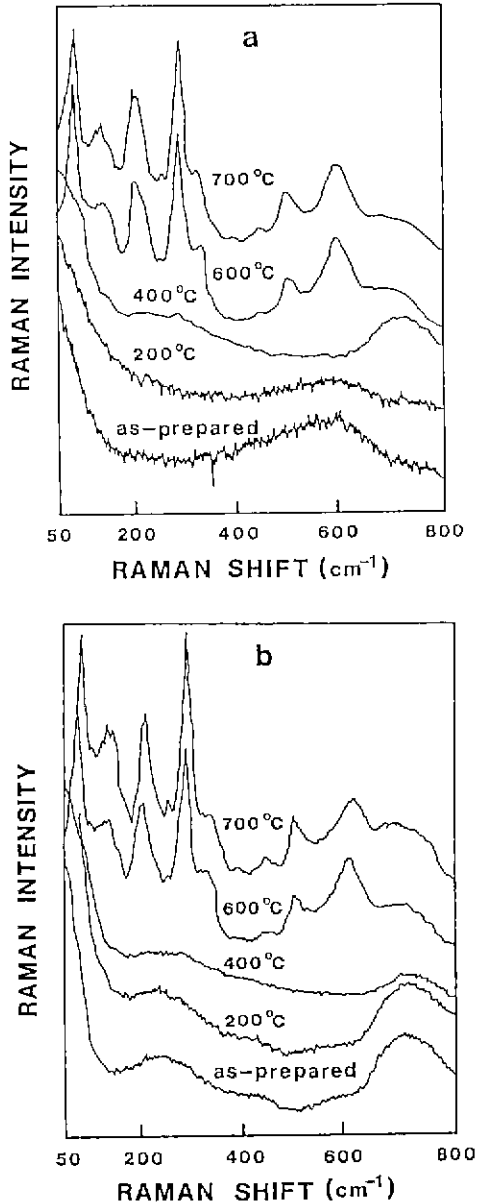


Fig. 3. Raman spectra from as-prepared and annealed samples, which were derived by (a) coprecipitation and (b) sol-gel processes.

the XRD patterns for the dried gel and coprecipitated powders when heated up to 600°C. The DTA run for the coprecipitated powders shows exothermic peaks at 330°C and 480°C. The XRD patterns of the powders heat-treated at 200°C, 400°C, and 500°C confirmed that the exothermic reaction at 480°C is associated with the

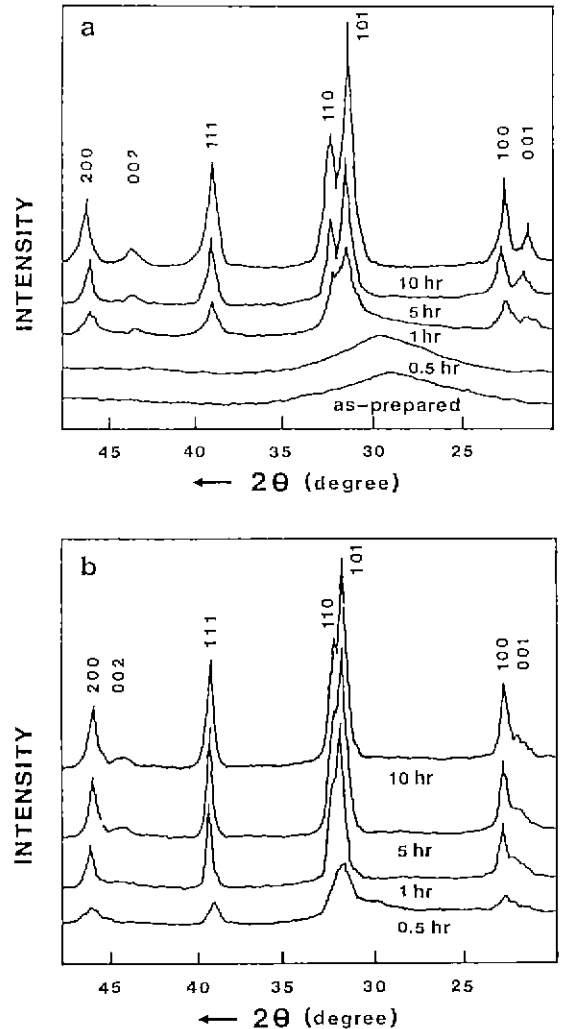


Fig. 4. Variation of X-ray diffraction patterns with calcination time; (a) coprecipitated PbTiO_3 , calcined at 400°C, (b) sol-gel derived PbTiO_3 , calcined at 450°C.

characteristic transformation from amorphous to crystalline PbTiO_3 (Fig. 2(a)). In case of the gel, only the exothermic peak at 475°C in the DTA curve is for the crystallization from amorphous, which is verified from the XRD patterns for the heat-treated gels shown in Fig. 2(b).

Raman spectra were obtained for samples in pellet form. Fig. 3 shows the spectrum at room temperature from the as-prepared coprecipitated and gel samples, together with those from heat-treated samples. A defi-

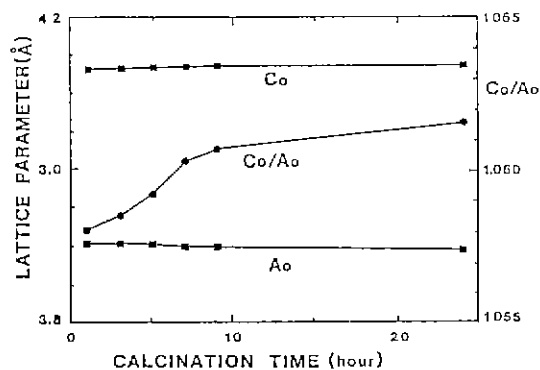


Fig. 5. Lattice parameters vs. calcination time for Pb-TiO₃ powders, calcined at 400°C.

nite change was observed when the samples were heated above the crystallization temperature. The crystalline PbTiO_3 samples exhibit an excitation called "soft-mode excitation" at $73\sim 80\text{ cm}^{-1}$. As the annealing temperature is higher, the soft mode shows hardening and the spectral pattern changes continuously to that of the crystalline state. The structure of the coprecipitates relaxes continuously to that of gel and crystalline, in turn.

Gurkovich and Blum¹³ have reported the preparation of monolithic amorphous lead titanate by a sol-gel process. They found a metastable intermediate phase in the material heat treated at 400°C for 6 hr, which was a mixture of the unknown phase and tetragonal PbTiO_3 . They reported a crystallization temperature of 470°C. In the present study, the crystallization temperatures of PbTiO_3 prepared by coprecipitation and sol-gel methods were about 480°C and 475°C, respectively.

Fig. 4 shows the XRD patterns for as-prepared PbTiO_3 powder and the powders calcined at 400°C and 450°C. The as-prepared coprecipitated powder and powders calcined at 400°C for 30 min are amorphous. The XRD pattern of the powders calcined at 400°C for 1 hr indicates the onset of crystallization. In the initial stage of calcination at 400°C, the diffraction peaks are very broad. After 10 hr of annealing a well-developed tetragonal PbTiO_3 diffraction pattern could be seen. The similar crystallization behavior of gel at 450°C could be observed in Fig. 4(b).

Yanaguchi *et al.*⁵⁾ have studied the crystallization of a sol-gel derived PbTiO_3 . They found a distorted cubic C' and a cubic C phase at 480°C and 580°C during heat-

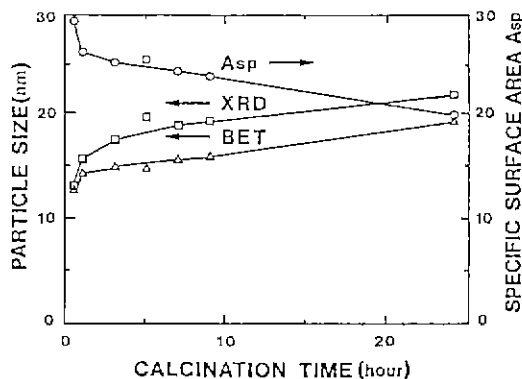


Fig. 6. Variation of particle size and specific surface area of the coprecipitated powders calcined at 400°C as a function of calcination time, measured by BET surface area analysis and X-ray diffraction patterns.

ing, respectively. The C' phase is stable at room temperature and has a larger cubic unit cell than the C phase. Only the C phase transforms reversibly to tetragonal T phase at the Curie temperature. In our study there was no indication of an additional cubic C' phase. From XRD patterns and DTA runs, it is clear that the as-prepared amorphous PbTiO_3 powder is partially transformed to tetragonal PbTiO_3 at 400~450°C. However the crystallization temperature of amorphous powder measured by DTA runs and the Curie temperature of PbTiO_3 are higher than 400°C. Lattice parameters of tetragonal PbTiO_3 calcined at 400°C were calculated from the XRD patterns, and shown in Fig. 5. The tetragonality (c/a) increased slightly with increasing calcination time. For the powder calcined at 400°C for 24 hr, $c=4.138\text{ \AA}$ and $a=3.898\text{ \AA}$ at room temperature.

Particle size of crystalline PbTiO_3 powders, calculated from BET specific surface area and the width of (111) peak in the XRD pattern, are shown in Fig. 6. The equivalent diameter of the particles was calculated from the specific surface area, by assuming the particles to be spherical and by measuring the density of the amorphous powders (about $7.2\sim 7.8\text{ g/cm}^3$). In the XRD method, the diffraction pattern of the powders calcined at 800°C for 1 hr was used as reference. The initial crystallite size of PbTiO_3 was about 12 nm and increased with the duration of calcination. The particle size was about 22 nm for the powders calcined at 400°C

for 24 hr.

Takashige *et al.*⁶⁾ investigated the crystallization process in rapidly solidified amorphous PbTiO_3 by studying the Raman spectra and dielectric properties. They observed that slightly above the crystallization temperature, the nucleation rate of the ferroelectric crystalline phase with short range order is very rapid, while the growth rate is slow. By suitable annealing at higher temperature, they were able to enhance the grain size and the extent of long range order. According to them, the ferroelectric crystal with short range order is nucleated rapidly. If the dimensions of this crystal increase above the correlation length to stabilize ferroelectricity, the long range order would be developed owing to the structural relaxation toward perfect crystalline state. Lee *et al.*⁸⁾ obtained similar results in their study for the crystallization of PbTiO_3 prepared by coprecipitation and sol-gel process.

4. Conclusions

Amorphous lead titanate powders have been prepared by coprecipitation and sol-gel methods, from a mixed solution of lead nitrate and titanium tetrachloride. The crystallization temperature at constant heating rate of $10^\circ\text{C}/\text{min}$ was observed to be 480°C for coprecipitates and 475°C for gel, which is in agreement with values reported in the literature for the crystallization of amorphous lead titanate prepared by other methods. The structure of the coprecipitated PbTiO_3 relaxes continuously to that of gel and crystalline, in turn. With sufficient annealing time, the coprecipitated powders and gel were found to crystallize at temperatures as low as 400°C for coprecipitates and 450°C for gel. yield-

ing a mixture of amorphous crystalline tetragonal phase.

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