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Effects of pH and H_2O_2 upon coprecipitated $PbTiO_3$ powders

Part II *Properties of calcined powders*

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$PbTiO_3$ was prepared by coprecipitation and calcination from mixed solutions of $TiCl_4$ and $Pb(NO_3)_2$. The effect of pH in the precipitation solution on the properties of calcined powders was studied by calcining coprecipitated precursor powders prepared at pH values between 8.00 and 10.50. The effects of H_2O_2 were studied by preparing $PbTiO_3$ powders from mixed solutions containing H_2O_2:$PbTiO_3$ ratios between 0:1 and 6:1. Synthesis of phase pure $PbTiO_3$ by coprecipitation and calcination is highly dependent upon the complex ionic equilibria dictated by the pH. The pH used for precipitation determines the types of crystalline phases formed from coprecipitated precursor powders. The rate at which amorphous precipitates transform to crystalline $PbTiO_3$ during calcination is also affected by both the pH and H_2O_2 additions. High purity (greater than 98%) $PbTiO_3$ with a rapid amorphous-to-crystalline transformation rate was obtained for H_2O_2:$PbTiO_3$ = 1.1:1, and pH = 9.65 to 9.75.

1. Introduction

The formation of crystalline $PbTiO_3$ from coprecipitated precursor powders followed by calcination is dependent upon the species contained in the precursor. In part I of this study [1] the properties of the precipitated precursor powders prepared from $Pb(NO_3)_2$ and $TiCl_4$ solutions were presented. This paper presents the powder properties after calcination of the coprecipitated powders prepared in part I and discusses how the properties of the precursor powders are related to the properties of the calcined powders. Since pH, speciation, and concentration of species influence the properties of precursor powders, the effects of these variables upon the calcined materials will be discussed.

2. Procedure for $PbTiO_3$ preparation and powder characterization

Two sets of coprecipitated powders were prepared from stock solutions of $Pb(NO_3)_2$ and $TiCl_4$ as described in the first part of this study [1]. The first set of powders was prepared with an H_2O_2:$PbTiO_3$ ratio of 1.1:1 but the five powders were prepared over different pH ranges of 8.00 to 8.20, 8.50 to 8.65, 8.90 to 9.15, 9.65 to 9.75, and 10.15 to 10.30. The second set of precipitated powders was prepared at a constant pH of 9.90 to 10.05 with the five powders in the set composed of H_2O_2:$PbTiO_3$ ratios of 0:1, 0.5:1, 1.1:1, 2:1, and 6:1. 3 g samples of each resulting powder were fired in covered alumina crucibles at 600 °C with a 5 h hold time. The samples were heated and cooled at 5 °C min^{-1}.

All calcined powders were analysed by X-ray diffraction* using Cu$K\alpha$ radiation at a scan rate of 1° 2θ min^{-1}. Integrated peak intensities were obtained at a scan rate of 0.1° 2θ min^{-1} with a coprecipitated $PbTiO_3$ powder (pH = 9.90 to 10.05, H_2O_2:$PbTiO_3$ = 1.1:1, calcined at 800 °C for 262 h) used as an external, fully crystallized standard. All samples were prepared as back loaded packed powder specimens. The specific surface areas of the calcined powders were obtained by a nitrogen adsorption technique.†

3. Results and discussion

3.1. Effects of pH on properties of calcined precipitates

Table I lists the crystalline phases within each of the calcined powders as determined by X-ray diffraction. X-ray diffraction patterns of the first set of powders prepared at constant H_2O_2:$PbTiO_3$ ratio 1.1:1 and various pH conditions exhibit formation of $PbTiO_3$, but a low intensity unidentified peak is observed at d = 0.294 nm (see Fig. 1). The intensity of the unidentified peak increases with decreasing pH values below 9.00. The pH value at which the intensity of the extraneous peak begins to increase corresponds to the

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* Scintag Pad V diffractometer, Santa Clara, California, USA.
† Quantachrome monosorb, model MS-12, Syosset, New York, USA.

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TABLE I Phases formed under various pH and H_2O_2 concentrations

pH	H_2O_2:$PbTiO_3$	Phases
8.00–8.20	1.1:1	$PbTiO_3$ + unknown (4%)
8.50–8.65	1.1:1	$PbTiO_3$ + unknown (3%)
8.90–9.15	1.1:1	$PbTiO_3$ + unknown (< 2%)
9.65–9.75	1.1:1	$PbTiO_3$ + unknown (< 2%)
9.90–10.05	1.1:1	$PbTiO_3$ + unknown (< 2%)
10.15–10.30	1.1:1	$PbTiO_3$ + unknown (< 2%)
9.90–10.05	0:1	$PbTiO_3$ + unknown (< 2%)
9.90–10.05	0.5:1	$PbTiO_3$ + unknown (< 2%)
9.90–10.05	2:1	$PbTiO_3$ + unknown (< 2%)
9.90–10.05	6:1	$PbTiO_3$ + unknown (< 2%)

pH for the solubility minimum and speciation change for the lead system.

Since the intensity of the unidentified diffraction peak does not increase at pH values above 9.00, it is likely that the formation of the second phase, causing the appearance of the diffraction peak, is not controlled merely by solubility of the lead. Also, if solubility did control the formation of the unidentified phase, aqueous lead or titanium species should have been observed in the filtrate of the precipitates. It was stated in part I that less than 1×10^{-5} mol^{-1} of lead and titanium species were observed in the filtrate solutions [1]. Change in the speciation of the lead from $HPbO_2^-$ and other complex lead hydroxo ions to Pb^{2+} below pH = 9.34 correlates with the appearance of the second phase. A study surveying a wider pH range than the present study is required to determine conclusively whether solubility of the lead species, change in the lead speciation, or a combination of these phenomena is responsible for the appearance of the second phase.

The specific surface area is plotted against pH for the calcined powders in Fig. 2. There is negligible change in the specific surface area with increasing pH, indicating that the calcined powders consist of particles of the same size, assuming similar morphologies for all particles. The ultimate particle size of the calcined powders is apparently independent of the specific surface area and particle size of the as-precipitated powders shown in part I, Fig. 5 [1].

Fig. 3 shows the concentration of crystalline $PbTiO_3$ as a function of pH for the calcined powders. Only the calcined powder prepared at pH = 9.65 to 9.75 exhibits 100% crystalline $PbTiO_3$. The precise maximum in the curve may occur anywhere between pH = 9.2 to 9.7. Again, the solubility minimum for the lead species corresponds with this finding. The fact that Fig. 3 exhibits an inverse relation to the solubility against pH curve for the lead system strongly suggests that the formation of crystalline $PbTiO_3$ is controlled by the solubility of the lead species.

The effect of pH upon the quantities of crystalline $PbTiO_3$ within the calcined powders cannot entirely be attributed to changes in rates of transformation from the amorphous to the crystalline state. As noted in Table I and Fig. 1 a small quantity of second phase was observed in the X-ray diffraction patterns. The increased quantity of unidentified second phase with pH values below 9.00 will correspondingly decrease the fraction of $PbTiO_3$ present in the powder specimens. If it is assumed that all the calcined powders consist of crystalline $PbTiO_3$ and the unidentified

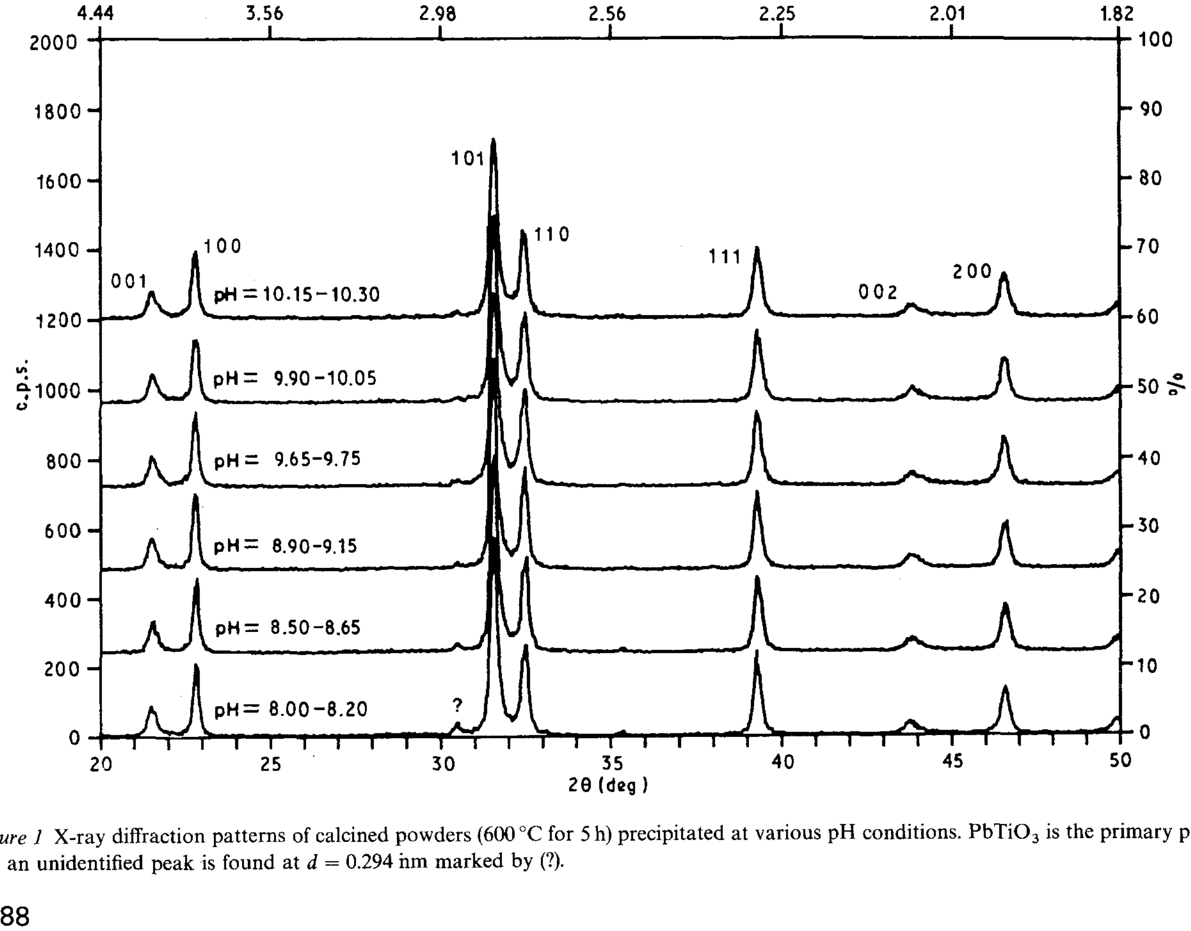

Figure 1 X-ray diffraction patterns of calcined powders (600 °C for 5 h) precipitated at various pH conditions. $PbTiO_3$ is the primary phase but an unidentified peak is found at d = 0.294 nm marked by (?).

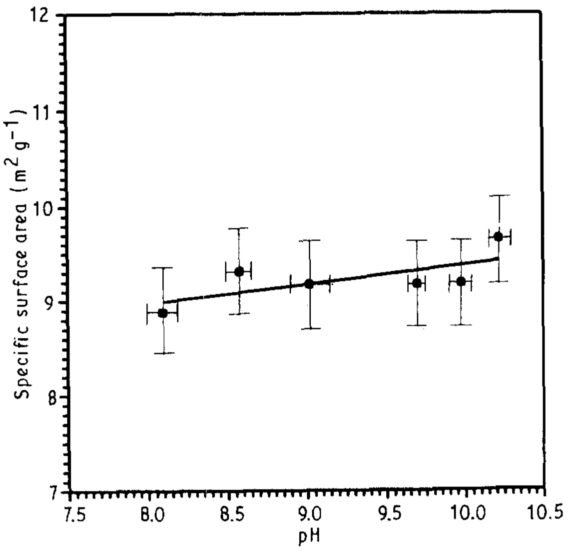

Figure 2 Effects of precipitation pH upon the specific surface area of calcined powders (600 °C for 5 h).

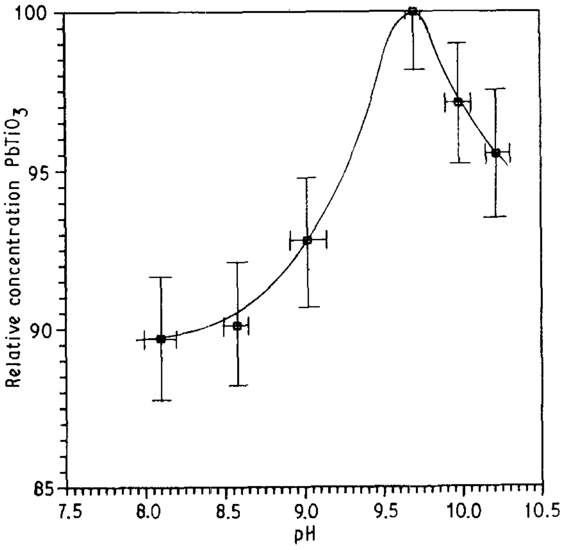

Figure 3 Effects of precipitation pH upon the concentration of crystalline $PbTiO_3$ in the calcined powders (600 °C for 5 h).

second phase, then formation of the second phase would appear to be controlled by the solubility of the lead species. As stated previously, however, a study covering a wider pH range is needed to determine whether the formation of the unidentified phase is controlled by lead solubility, changes in speciation of the lead, or a combination of these phenomena. Both the transformation rate of the amorphous powder and the formation of the second phase are likely to contribute to the pH dependency of the quantity of crystalline $PbTiO_3$ observed in calcined powders.

3.2. Effects of H_2O_2 upon properties of calcined precipitates

All X-ray diffraction patterns of the calcined powders from set two, with increasing H_2O_2:$PbTiO_3$ ratios, exhibited primarily $PbTiO_3$ peaks with less than 2% by weight unidentified second phase. This finding indicates that H_2O_2 additions do not affect the crystalline phases present in the calcined powders. Although the type of crystalline phases formed from the precipitates is not influenced by the H_2O_2 additions, the widths and intensities of the diffraction peaks change with increasing H_2O_2 concentration (see Fig. 4).

The change in specific surface area of the calcined powder as a function of H_2O_2 concentration during precipitation is shown in Fig. 5. There is a minimum in the specific surface area at an H_2O_2:$PbTiO_3$ ratio 1.1:1. The as-precipitated powders described in the first part of the study [1] exhibited a maximum in the specific surface area at H_2O_2:$PbTiO_3$ = 1.1:1. The powders with the highest specific surface areas before calcination have the lowest specific surface areas after calcination. Therefore, the powder prepared with H_2O_2:$PbTiO_3$ = 1.1:1 exhibits the highest growth rate during calcination which is consistent with the large surface area of the precipitate prior to calcination.

In Fig. 6, the X-ray diffraction integrated 111 peak intensities were used to determine the concentration of crystalline $PbTiO_3$ relative to an external $PbTiO_3$ standard. The concentration of $PbTiO_3$ displays a maximum as a function of increasing H_2O_2 concentration. The results indicate that the powder prepared with H_2O_2:$PbTiO_3$ = 1.1:1 contains the highest concentration of crystalline $PbTiO_3$ and therefore transforms from the amorphous to the crystalline state at the fastest rate. Comparison of the data in Figs 5 and 6 supports the contention that the precipitate prepared with H_2O_2:$PbTiO_3$ = 1.1:1 has the highest nucleation and growth rate during transformation from the amorphous to the crystalline state.

The reason why H_2O_2 affects the nucleation and growth rate of crystalline $PbTiO_3$ during transformation from the amorphous precipitates may be due to several factors. First, since the free energy for the transformation to the crystalline state is partly dependent upon the reduction of surface area [2, 3], the amorphous powders exhibiting the highest specific surface area will have the largest driving force for transformation. Therefore, the effect of H_2O_2 upon the nucleation and growth rates may only be an artifact due to the influence of H_2O_2 on the specific surface area of the precipitated powders. Evidence for this is given by the correlation between the maximum in the specific surface area plotted against H_2O_2:$PbTiO_3$ for the as-precipitated powders (see Part I, Fig. 3) [1], and the maximum for concentration of $PbTiO_3$ against H_2O_2:$PbTiO_3$ (Fig. 6). This correlation in maxima suggests that the powder prepared at H_2O_2:$PbTiO_3$ = 1.1:1 exhibits the highest amorphous to crystalline transformation rate because it exhibits the highest specific surface area, and therefore, the highest surface free energy change upon transformation and growth.

Another reason why H_2O_2 influences the nucleation and growth rates of the crystalline $PbTiO_3$ may be due to the effect that H_2O_2 has on the anionic species present in the precipitates. As found in Part [1], carbonates are formed when no H_2O_2 is added to the system, and changes in structural water content may occur at high H_2O_2 concentrations. Therefore,

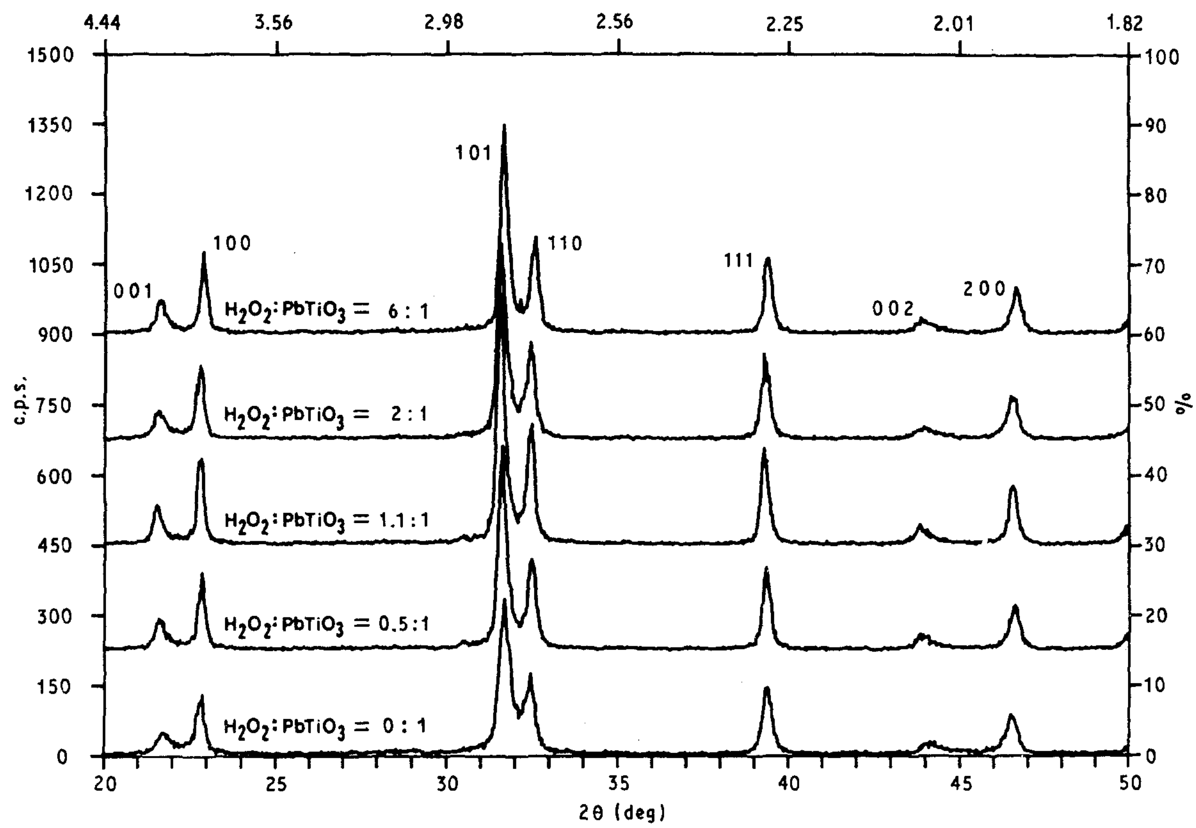

Figure 4 X-ray diffraction patterns for calcined precipitates (600 °C for 5 h) prepared with increasing H_2O_2 concentration. Pure $PbTiO_3$ is observed for each of the powders.

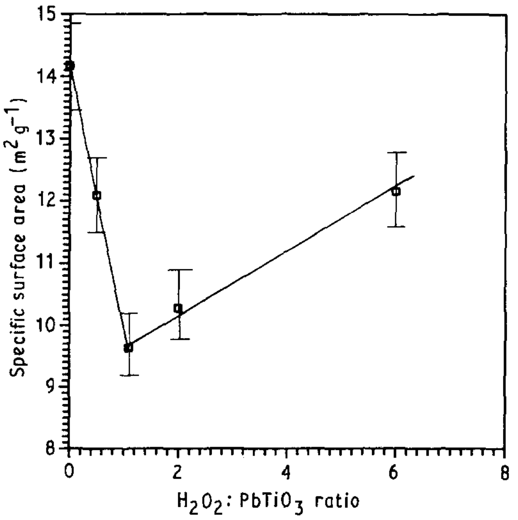

Figure 5 Specific surface area of calcined precipitates (600 °C for 5 h) with increasing H_2O_2 concentration.

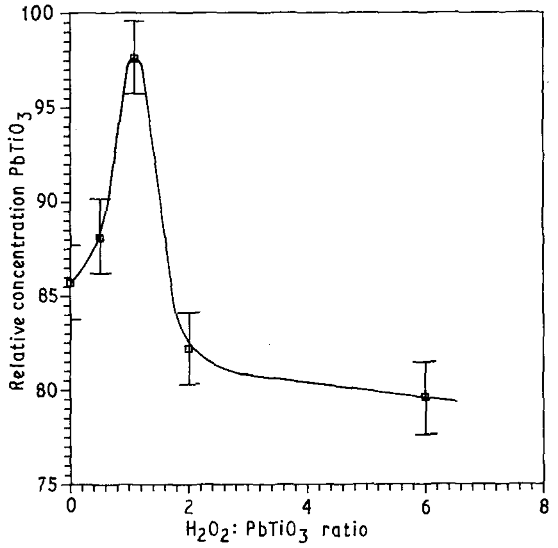

Figure 6 Effects of H_2O_2 concentration upon concentration of crystalline $PbTiO_3$ in calcined precipitates (600 °C for 5 h).

the pronounced effect that H_2O_2 has upon the transformation of the amorphous precipitates to crystalline $PbTiO_3$ is most likely due to a combination of the effects that H_2O_2 has on both the specific surface area of the precipitates and the anionic species contained in the precipitates.

4. Conclusions

Formation of crystalline $PbTiO_3$ in powders prepared by the coprecipitation–calcination process is found to be highly dependent upon the solubility and speciation of lead and titanium and their chemical derivatives. Both solubility and speciation are dependent upon concentration and pH, and therefore, both concentration and pH will affect the phases formed during the precipitation–calcination process. The final crystalline phases are not affected by H_2O_2 additions. Pure $PbTiO_3$ is not obtainable at pH below 9.00 because of the appearance of a persistent second phase. Above pH 9.00 greater than 98% by weight pure $PbTiO_3$ is formed but the rate at which the amorphous precipitates transform to crystalline $PbTiO_3$ exhibits a maximum as a function of both pH and H_2O_2 concentration. The maximum transformation rate from amorphous precipitates to greater than 98% pure crystalline $PbTiO_3$ is with H_2O_2:$PbTiO_3$ = 1.1:1 and pH = 9.65 to 9.75.

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