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Effects of pH and H_2O_2 upon coprecipitated $PbTiO_3$ powders:

Part I *Properties of as-precipitated powders*

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The properties of precipitated materials are highly dependent upon the complex ionic equilibria of the species in the solutions used for precipitation. Concentration, temperature, and pH dictate the complex species present within aqueous systems, and therefore affect the final precipitate properties. This paper discusses the effect of pH on the properties of $PbTiO_3$ precursor powders prepared by adding stoichiometric mixtures of $TiCl_4$ and $Pb(NO_3)_2$, in aqueous solution, to NH_4OH solutions. Several powders were prepared between pH 8.00 and 10.50. The pH does not affect the amorphous structure, but does have a pronounced effect upon the specific surface area and growth mechanisms of the precipitates.

Since previous studies indicated that hydrogen peroxide (H_2O_2) affects the hydroxylation of the precipitated powders, the effect of H_2O_2 concentration on the precipitate properties was also studied. Several precipitates were prepared from solutions containing H_2O_2 : $PbTiO_3$ ratios between 0 : 1 and 6 : 1. When H_2O_2 was not added to the solutions used for precipitation, atmospheric CO_2 dissolved in solution caused precipitation of carbonate species. Thus, addition of the H_2O_2 to the solutions inhibited precipitation of the carbonates.

1. Introduction

By using chemical solution techniques for the preparation of multi-component powders, it is possible to produce high purity, homogeneous materials in which stoichiometry can easily be controlled [1]. The preparation of high purity fine grain size $PbTiO_3$ via solution techniques has been demonstrated by several workers who have used both sol–gel [2, 3] and coprecipitation techniques [4, 5]. These authors have used a variety of starting materials for the preparation of $PbTiO_3$ powders, and have therefore obtained varying results with respect to particle size, reactivity, and other powder properties.

The objective of the present study was to determine the effects that pH and H_2O_2 have upon the characteristics of $PbTiO_3$ prepared from mixed solutions of $TiCl_4$ and $Pb(NO_3)_2$. The first part of the study, presented in this paper, discusses the affects of pH and H_2O_2 upon the characteristics of as-precipitated $PbTiO_3$ precursor powders. Properties of the calcined precipitates with relation to pH and H_2O_2 additions will be discussed in the second part of the study [6].

The properties of a precursor powder obtained by solution techniques is highly dependent upon the chemical species and concentration of species present in the system. Effects due to H_2O_2 additions to the starting solution of $Pb(NO_3)_2$ and $TiCl_4$ were studied because H_2O_2 additions have been reported to suppress the formation of hydroxides [7]. Since solubility and the nature of complex species present in solution are dependent on pH, it is likely that the pH at which the coprecipitation process occurs controls the species that are precipitated. Although coprecipitation is a dynamic process, that is often dominated by kinetic aspects, some insight can be obtained by first looking at the equilibrium chemistry of the species in the aqueous system used for the coprecipitation.

The solubility product of a chemical system provides one with a quantitative measure of the equilibrium relation between ions in solution and the solid species consisting of the same type of ions. Difficulties in determining the value of the solubility product are, however, common and errors in the reported values can be as high as 10^5. Also, it cannot be stressed enough that the solubility product can apply quantitatively only to equilibrium conditions. Therefore, when the solubility product is applied to systems with high ionic strengths, systems containing extrinsic species, or systems that are not at equilibrium, even use of the solubility product as a qualitative tool becomes questionable. Furthermore, some authors believe that application of the solubility product, even qualitatively, to systems that form gelatinous or amorphous precipitates is erroneous [8].

Although $Pb(NO_3)_2$ and $TiCl_4$ have been used to produce a gelatinous $PbTiO_3$ precursor precipitate which is far from equilibrium, it is still instructive to examine the solubility products in this coprecipitation system keeping in mind the above reservations. While solubility products of the various species involved may not indicate the precise species that will be precipitated, it may give a clue to the

TABLE I Aqueous species present during coprecipitation process

Precursor	Aqueous species
$TiCl_4$	Ti^{4+} (hydrated complex) Cl^-
$Pb(NO_3)_2$	Pb^{2+}, NO_3^-, $HPbO_2^-$
H_2O_2	H_2O_2
NH_4OH	NH_4^+, OH^-
CO_2 (from air)	HCO_3^-, CO_3^{2-}

types of bonding that can be formed in the solid precipitates.

1.1. Solubility of species involved in coprecipitation process

The species involved in the coprecipitation process are given in Table I, and possibilities for compounds that may be present in the coprecipitated powders are listed in Table II according to decreasing calculated solubility product. Calculated solubility products were determined from thermodynamic data [9, 10]. Experimental values of the solubility product [11] generally agree with the calculated values within one to two orders of magnitude. From Table I it can be seen that there are several species that can contribute to the ionic strength of the solution; this adds to the complexity in predicting the speciation of any one ion or ionic complex. The large number of possible products obtainable from the aqueous species appears to make it impossible to predict the type of precipitate that will form, but a prediction for the product of the coprecipitation can be limited. Since $PbCl_2$ and the lead compounds containing nitrates exhibit relatively high solubilities compared to the other compounds, they are unlikely to form, and any residual chloride or nitrate ion should wash from the precipitate. In order to make any further predictions and to understand the coprecipitation process, one must take a closer look at the aqueous chemistry of titanium, lead, and the affects of atmospheric CO_2.

1.2. Aqueous chemistry of titanium species

The Ti^{4+} ion only occurs in solution as a complex species over any practical pH range (pH 1 and higher). Since Ti^{4+} has a high charge-to-size ratio, it exhibits highly acidic properties and therefore only hydrolysed derivatives are observed in aqueous solutions. The equilibria is believed to be represented by reactions of the type [12]

$$[Ti(H_2O)_4(OH)_2]^{2+} + H_2O \leftrightarrow [Ti(H_2O)_3(OH)_3]^+ + H_3O^+$$

in dilute non-complexing acidic solutions. By adding a base to the system the hydrous oxide of titanium is precipitated as follows

$$[Ti(H_2O)_3(OH)_3]^+ + H_2O \leftrightarrow [Ti(H_2O)_2(OH)_4] + H_3O^+$$

From this *equilibrium* equation, taking into consideration that other hydrolysed derivatives occur, and that the species cited above may not be the most thermodynamically stable of these adducts, it is found that the hydrous oxide of titanium will precipitate over a wide basic pH range. Some uncertainty over the exact species present as a function of pH still exists and this may be due in part to the observation that aqueous Ti^{4+} exhibits formation of polymeric structures with oxygen bridging between the titanium and hydroxyl termination groups [12, 13].

1.3. Aqueous chemistry of lead species

Pourbaix has described the speciation and solubility of lead in aqueous systems and has found that it is highly dependent upon pH [14]. His calculations are limited in that hydroxo complexes are ignored. Pourbaix provides a useful set of solubility curves for red PbO (tetragonal), yellow PbO (orthorhombic), and $Pb(OH)_2$. All three solids show a minimum solubility at pH = 9.34 with $Pb(OH)_2$, yellow PbO, and red PbO exhibiting respectively lower solubilities and higher thermodynamic stabilities. Below pH = 9.34 the lead becomes soluble as the Pb^{2+} species and at pH greater than 9.34 the plumbate ion ($HPbO_2^-$) becomes the soluble species. All three of the solid lead species undergo similar complex speciation reactions, thus their thermodynamic stability is also similar. However, in the coprecipitation process under study, the high concentrations of extrinsic species (such as Cl^- and NO_3^-) may alter the relative stability of the solid lead species. Extrinsic species are also likely to affect the nucleation and growth process of each solid species

TABLE II Possible precipitation products

Compound solubility reaction	Calculated solubility product	Experimental solubility product
$Pb(NO_3)_2 \Leftrightarrow Pb^{2+} + 2NO_3^-$	1.3×10^{-1}	5.9
$Pb(OH)NO_3 \Leftrightarrow Pb^{2+} + NO_3^- + OH^-$	1.3×10^{-2}	2.0×10^{-5}
$PbCl_2 \Leftrightarrow Pb^{2+} + 2Cl^-$	1.6×10^{-5}	5.7×10^{-5}
$PbCO_3 \Leftrightarrow Pb^{2+} + CO_3^{2-}$	3.2×10^{-14}	4.0×10^{-11}
PbO (yellow) $+ H_2O \Leftrightarrow Pb^{2+}\ 2OH^-$	7.1×10^{-16}	1.1×10^{-12}
PbO (red) $+ H_2O \Leftrightarrow Pb^{2+} + 2OH^-$	4.7×10^{-16}	1.6×10^{-13}
$Pb(OH)_2 \Leftrightarrow Pb^{2+} + 2OH^-$	1.1×10^{-20}	1.1×10^{-20}
$TiO(OH)_2 \Leftrightarrow TiO^{2+} + 2OH^-$	3.6×10^{-30}	7.9×10^{-54}
TiO_2 (anatase) $+ H_2O \Leftrightarrow TiO^{2+} + 2OH^-$	1.8×10^{-40}	unknown
$2PbCO_3 \cdot Pb(OH)_2 \Leftrightarrow 3Pb^{2+} + 2CO_3^{2-} + 2OH^-$	9.0×10^{-48}	1.4×10^{-40}
$PbTiO_3$	unknown	unknown
$PbTi_3O_7$	unknown	unknown
$Pb_2Ti_2O_6$	unknown	unknown

from the aqueous solution. It can be deduced from the listed solubility products that red PbO, yellow PbO and $Pb(OH)_2$ are all likely candidates for precipitation if the pH of the aqueous system is maintained near the solubility minimum for the lead system.

The occurrence of the solubility minimum in the lead system also may have a significant effect upon the stoichiometry of a coprecipitate incorporating lead and titanium. The hydrous oxide of titanium is formed readily over a wide range of basic conditions, but significant amounts of lead may remain in the solution if the pH is not maintained close to the solubility minimum at 9.34. Accordingly, the stoichiometry for formation of $PbTiO_3$ from the precipitate should be attainable if the pH is maintained near the lead solubility minimum, but deviation from this pH may allow the formation of other lead and titanium compounds.

1.4. Affects of atmospheric carbon dioxide

Since lead carbonate and basic lead carbonate are highly insoluble in high pH solutions and because CO_2 makes up a significant part of the atmosphere, the equilibrium for carbonate containing species must also be considered. Carbon dioxide from the air behaves as a Lewis acid and reacts with water to form carbonic acid, and associated protonated carbonates, particularly under high pH conditions. The carbonic acid dissociates in solution to form aqueous carbonate and basic carbonate species that can react with the lead in solution. The concentration of each type of carbonate species is determined by the pH of the solution as can be calculated from the pK_a values for $H_2CO_3(pK_a = 4.45 \times 10^{-7})$ and $HCO_3^-(pK_a = 4.69 \times 10^{-11})$ [15]. At the minimum solubility pH for the lead system (i.e., pH 9.34), the HCO_3^- ion is predominant, but the high concentration of ionic species used in the coprecipitation process may shift this equilibrium to produce substantial concentrations of both HCO_3^- and CO_3^{2-} species [15, 16].

According to Todd and Perry, CO_2 plays an important role in the solubility equilibria of the aqueous lead system and they have stated that "considerable confusion persists in the literature regarding the distinction between lead hydroxide and basic lead carbonate, principally because the latter is encountered in reactions where lead hydroxide is the anticipated product" [17]. This statement by Todd and Perry is supported by the fact that the solubility product for $2PbCO_3 \cdot Pb(OH)_2$ is much less than the solubility product for $Pb(OH)_2$ (see Table II). From this evidence, the lead carbonate and basic lead carbonate species must be considered as possible precipitation products for the system being investigated.

1.5. Effects of H_2O_2 on titanium and lead chemistry

Several workers have prepared $PbTiO_3$, PZT, and PLZT from $Pb(NO_3)_2$ and $TiCl_4$ precursors, with the addition of H_2O_2. These studies suggest that the H_2O_2 additions suppress the hydrolysis of the Ti^{4+} species and prevent the presence of $Pb(OH)_2$ in the precipitate due to a dehydration reaction in the presence of the H_2O_2 [7, 18]. No conclusive evidence has been advanced to support the proposal that H_2O_2 suppresses formation of hydroxides and this hypothesis becomes even more questionable when considering the possible affects of the carbonate, and basic carbonate species.

When H_2O_2 is added to an aqueous solution containing Ti^{4+}, formation of complex species are observed which change according to the pH of the solution. In acidic solutions, Ti^{4+} and H_2O_2 react to give a complex exhibiting a red–brown colour, but there is much confusion over the form of the coloured species. At pH < 3 the species has been described as $[Ti(O_2) \cdot 3H_2O]^{2+}$, $[Ti(H_2O_2)]^{4+}$, and $[Ti(OH)_2 \cdot H_2O_2]^{2+}$ and in the presence of aqueous anions has also been described as an anionic complex. For solutions with pH between 3 and 6, the species $[Ti(O_2)OH \cdot 2H_2O]^+$, $[Ti(O_2H)]^{3+}$, and $[Ti(O_2)]^{2+}$ have been proposed. Although the exact species present in acidic solutions has not been agreed upon, it is generally accepted that the species contains one peroxy group to each titanium atom. In neutral solutions, a yellow species consisting of one peroxy group for each titanium atom is observed and a yellow solid can be obtained that contains either one or two molecules per formula unit. At pH values greater than pH 10 a colourless species is observed with the proposed formula of either $[Ti(O_2)_2(OH)_2]^{2-}$ or $[Ti(O)(O_2)(OH)_2]^{2-}$ [19].

Lead oxide has been shown to be catalytic in the decomposition reaction of H_2O_2 indicating that the lead has some interaction with the H_2O_2 species during the coprecipitation process [20]. Exactly how the peroxide affects the coprecipitation process is unknown and is considered in the present study.

After considering the above discussion, a list of the most likely compounds to be formed from the coprecipitation process can be stated. If the lead and titanium species precipitate as independent compounds, the titanium species are most likely to precipitate as the hydrous oxide. The lead species may precipitate as either red PbO, yellow PbO, $Pb(OH)_2$, $2PbCO_3 \cdot Pb(OH)_2$, or $PbCO_3$. If the lead and titanium precipitate as a homogeneous solid, $PbTiO_3$ would be the most likely form if the lead and titanium are mixed in a 1 : 1 ratio and the pH of the aqueous medium is maintained close to pH 9.34. Other lead titanate phases may form if the pH is not maintained at the solubility minimum for the lead system. Since the coprecipitation process is not at equilibrium, it is unlikely that crystalline products are formed. Amorphous or gelatinous derivatives of these compounds are most likely to form.

2. Procedure for $PbTiO_3$ coprecipitation and powder characterization

In order to study the effects of H_2O_2 additions and pH upon the properties of coprecipitated $PbTiO_3$, the formation of two sets of precipitates were required for study. The first set of precipitates was made at a constant pH while varying the H_2O_2 concentration and the second set of precipitates was prepared at a constant H_2O_2 concentration and varying pH. Details of the coprecipitation process are summarized in Fig. 1. A stock solution of $TiCl_4$ was prepared by adding

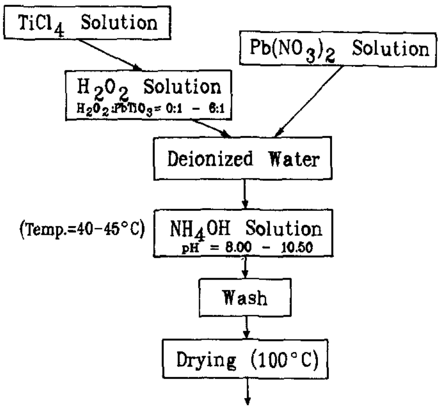

Figure 1 Diagram of coprecipitation process for $PbTiO_3$.

$TiCl_4$* to chilled deionized water. The concentration of the $TiCl_4$ solution was determined by both chemical and gravimetric techniques and the solution had a concentration of $2.65\,mol\,l^{-1}$. A $1.00\,mol\,l^{-1}$ stock solution was prepared from $Pb(NO_3)_2$.[†]

Preparation of the set of precipitates with varying H_2O_2 concentration is described first. $TiCl_4$ solution, 9.43 ± 0.02 ml and concentration $2.65\,mol\,l^{-1}$, was added to 500 ml deionized water to give 0.025 moles of hydrolysed Ti^{4+} in solution. Hydrogen peroxide[‡] was then added to the dilute $TiCl_4$ solution. Lead nitrate solution, 25.00 ± 0.02 ml and concentration $1.00\,mol\,l^{-1}$, was added to the hydrolysed Ti^{4+} solution following the H_2O_2 addition to give a mixed solution with a 1:1 stoichiometric ratio of lead to titanium. The mixed solution was diluted with deionized water to give a total volume of 1000 ml that was heated and maintained at 43 ± 2° C in order to dissolve any lead chloride that was precipitated during preparation of the mixed solution. The heated solution was pumped at a rate of $10\,ml\,min^{-1}$ into a three-neck flask containing 500 ml NH_4OH[§] solution at pH = 9.90 to 10.05 with a temperature maintained at 43 ± 2° C. During the coprecipitation process, the pH of the solution in the three-neck flask was maintained at pH = 9.90 to 10.05 by adding NH_4OH solution. The solution in the three-neck flask was constantly stirred. This procedure was repeated five times using different concentrations of H_2O_2. Five precipitates were therefore prepared containing H_2O_2 : $PbTiO_3$ molar ratios of 0:1, 0.5:1, 1.1:1, 2:1 and 6:1.

The set of precipitates with varying pH were prepared by holding the mixed solution H_2O_2 : $PbTiO_3$ ratio constant at 1.1:1. Five precipitates were then prepared from this type of mixed solution by following the same mixing procedure described earlier, but the pH of the solution in the three-neck flask was maintained within a different pH range for each of the five precipitates. The five pH ranges used to prepare the precipitates were 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.

After the precipitate was formed in the three-neck flask, the supernatant and precipitate were separated by vacuum filtration. The precipitates were filtered until they exhibited a gelatinous consistency to ensure easier dispersion for subsequent washing. After filtration, the wet precipitate was redispersed in 1000 ml deionized water at 25° C and stirred for 15 min. This washing procedure was repeated five times with the precipitates vacuum filtered after the final wash until no further solution could be withdrawn from the precipitates. The washed precipitates were then dried at 100° C for 24 h.

Samples of the supernatant solution from each wash and filtration step were filtered a second time using $- 0.45\,\mu m$ filter paper and the solutions were analysed for the concentration of aqueous lead (analysed at 405.8 nm) and titanium (analysed at 334.9 nm) using a d.c.-plasma emission spectrometer[¶]. The concentration of Cl^- and NO_3^- in the filtrate was also monitored using ion chromatography[**]. An additional test to evaluate the concentration of residual Cl^- and NO_3^- within the washed precipitates was also performed. A 0.3 g sample of dried as-precipitated powder was placed in 50 ml deionized water and boiled for 1 h. The solution was then separated from the boiled powder and the filtrate was tested for Cl^- and NO_3^- using ion chromatography. Energy dispersive spectroscopy was also used to determine whether residual Cl^- remained in the washed precipitates[††].

The as-precipitated powders were analysed by X-ray diffraction[‡‡] using CuKα radiation at a scan rate of $1°\,2\theta\,min^{-1}$. All samples were prepared as back loaded packed powder specimens. The specific surface area of the as-precipitated powders was obtained by a nitrogen single-point adsorption technique[§§]. Infrared spectra of the as-precipitated powders were obtained from 200 mg KBr pellets containing 1 mg of the powder specimen[¶¶].

3. Results and discussion

3.1. Initial observations of mixed solution and precipitate properties

Previous papers on the coprecipitation of $PbTiO_3$ have neglected a thorough description of the colour and pH changes that occur during the preparation process.

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[*] Aldrich Chemical Co., Titanium (IV) Chloride 99.9%.

[†] Aldrich Chemical Co., Lead (II) Nitrate 99 + % A. C. S. reagent grade.

[‡] Aldrich Chemical Co., Hydrogen peroxide 30% by weight solution in water, A. C. S. reagent grade.

[§] Aldrich Chemical Co., Ammonium Hydroxide A. C. S. reagent grade.

[¶] Spectrametrics Inc. Spectra Scan III, Andover, Massachusetts, USA.

[**] Dionex, model 2011, Sunnyvale, California, USA.

[††] Philips EM 420 transmission electron microscope with a LINK EDS attachment, Mahwah, New Jersey, USA.

[‡‡] Scintag Pad V diffractometer, Santa Clara, California, USA.

[§§] Quantachrome monosorb, model MS-12, Syosset, New York, USA.

[¶¶] IBM FTIR, Model 98 with a globar source, Danbury, Connecticut, USA.

TABLE III pH and colour changes during mixed solution preparation

Solution contents	pH	Colour
$TiCl_4$ + 500 ml H_2O	1.5	colourless
$TiCl_4$ + 500 ml H_2O + H_2O_2	1.5	red-brown
$TiCl_4$ + 500 ml H_2O + H_2O_2 + $Pb(NO_3)_2$	1.5	red-brown
$TiCl_4$ + 1000 ml H_2O + H_2O_2 + $Pb(NO_3)_2$	1.8	red-brown

Since pH and colour changes of aqueous solutions are sound indications of reactions in solution, these two properties have been observed and reported for the coprecipitation process.

While the mixed solution containing $TiCl_4$, H_2O_2, and $Pb(NO_3)_2$ was prepared, the pH and colour were monitored and the results of the observations are given in Table III. When the $TiCl_4$ stock solution is added to the water, a clear solution is obtained and the pH is lowered. This is due to the acidic nature of the titanium complex that hydrolyses in aqueous solution. On addition of the H_2O_2 to the diluted $TiCl_4$ solution, the colour of the solution is changed to a reddish brown but the pH remains constant. The colour change upon addition of the H_2O_2 indicates that the H_2O_2 complexes with the Ti^{4+}, as described earlier, but does not greatly alter the acid concentration of the aqueous titanium complexes. Addition of $Pb(NO_3)_2$ to the system does not alter the pH balance or the colour of the solution; therefore, no predictions can be made about the species present in the mixed solution other than those described previously for the aqueous lead system. Since the pH for the mixed solution is below the solubility minimum described earlier for the aqueous lead oxide system, Pb^{2+} should be the predominant species. Some $PbCl_2$ is observed to form before the mixed solution is diluted to its final volume but the $PbCl_2$ precipitate dissolves after the final dilution is complete.

When the mixed solution is added to the NH_4OH solution an orange precipitate is formed that after washing and drying is a red-brown powder on crushing. These observations are consistent for all of the powders prepared under the various pH and H_2O_2 conditions, except for the powder prepared with no H_2O_2 addition. The precipitate formed without the H_2O_2 addition was pale yellow in colour with the washed, dried and crushed powder also exhibiting a pale yellow colour.

The red-brown colour of the powders prepared with the H_2O_2 additions suggests that the Pb-O bonding within the dried precipitate may be similar to the Pb-O bonds found within red PbO. Bonding similar to that found in yellow PbO may cause the appearance of the yellow colour in the powder prepared without an H_2O_2 addition. The change in powder colour upon addition of H_2O_2 to the mixed starting solution indicates that H_2O_2 has a definite effect upon the bond types and structure exhibited by the precipitate.

3.2. Determination of chemical purity of precipitates

Chemical analysis of the supernatant solution collected during filtration and washing of the precipitates indicated concentrations of less than $1 \times 10^{-5}\,mol\,l^{-1}$ for both lead and titanium species. This indicates that the cations were almost completely precipitated from solution with the concentration of aqueous lead and titanium species dictated by the solubility limits of the precipitated solid. This also implies that no significant leaching of the cations occurred from washing the precipitates and that the precipitates contained stoichiometrically equivalent amounts of Pb^{2+} and Ti^{4+} species.

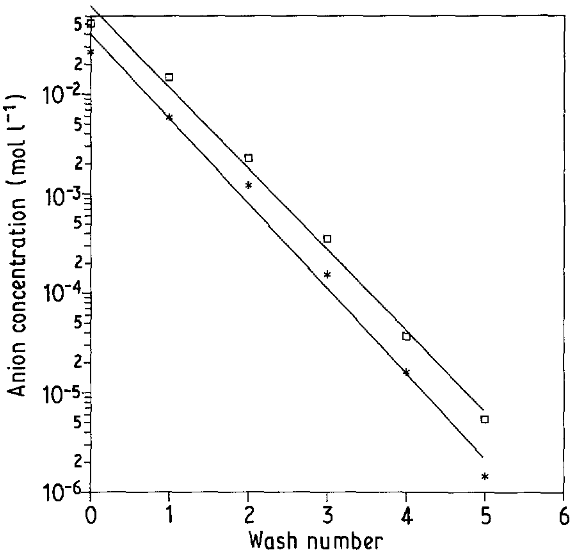

Figure 2 Decrease in concentration of Cl^- (□) and NO_3^- (*) in filtrate of precipitates with increased washing.

A typical curve for the concentration of Cl^- and NO_3^- as a function of wash number is given in Fig. 2. After the powders were washed five times, less than $1 \times 10^{-5}\,mol\,l^{-1}$ of either Cl^- or NO_3^- was detected in the supernatant solution. It is believed that the concentration of these anions in the precipitates are similar to the concentrations observed in the supernatant solution. It was determined that the powders contained at most 0.1 mol% each of Cl^- and NO_3^- species after washing. Energy dispersive spectroscopy of the precipitates indicated that only lead and titanium were present in the powders, therefore confirming that the residual Cl^- concentration in the washed precipitates was negligible.

3.3. Effects of H_2O_2 additions upon precipitate properties

To gain information about the effects of H_2O_2 upon the precipitation process, the properties of as-precipitated powders prepared at various H_2O_2 concentrations and constant pH were determined. X-ray diffraction patterns of the as-precipitated powders made with the various $H_2O_2 : PbTiO_3$ ratios with pH held relatively constant over the range pH = 9.90 to 10.05 indicate that the as-precipitated powders are amorphous with negligible differences as a function of H_2O_2 concentration. All the diffraction patterns display broad amorphous peaks centred around $d \approx 0.3$ nm and $d \approx 0.18$ nm which may be related to the Pb-O and Ti-O bonding distances, respectively.

The infrared absorption spectra for the as-precipitated powder prepared with no H_2O_2 addition to the

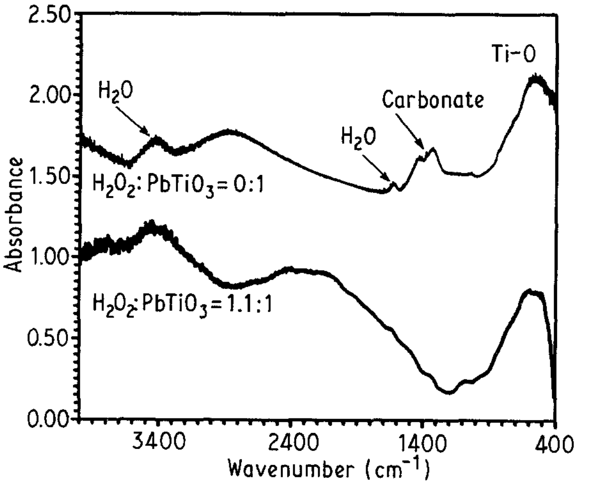

Figure 3 Infrared spectra of as-precipitated powders. The top spectra indicates the formation of carbonates in powders prepared without H_2O_2, and the bottom spectra is typical for powders prepared with H_2O_2 that suppresses carbonate formation.

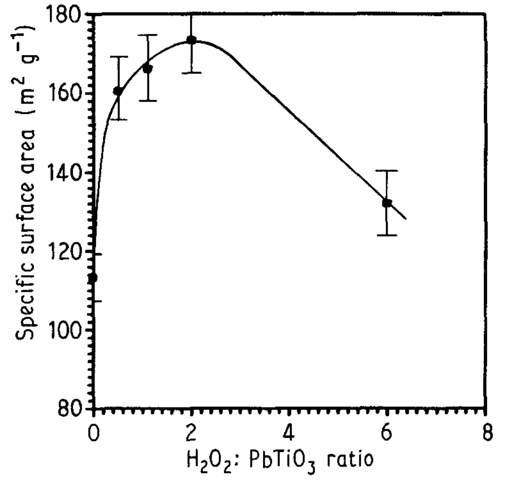

Figure 4 Influence of H_2O_2 upon the specific surface area of as-precipitated powders.

mixed solution was found to be quite different from the powders prepared with H_2O_2 additions. In Fig. 3, the bottom curve shows the typical absorption spectra for the powders prepared with H_2O_2 additions while the top curve is the spectra for the powder prepared without the H_2O_2 present. One of the most obvious differences between the two curves is the absorption peak observed between 1500 and 1200 (cm^{-1}) wavenumbers for the powder prepared without H_2O_2 that is not present in the spectrum for the powder prepared with H_2O_2. This absorption peak is characteristic of either carbonate or nitrate species [21]. Since the nitrate species washed freely from the precipitate, it is likely that the absorption peak between 1500 and 1200 (cm^{-1}) wavenumbers is due to carbonate species.

In the powder prepared without the H_2O_2 addition, the appearance of carbonate species in the precipitates agrees with the observations made by Todd and Perry [17], described previously. They stated that lead basic carbonate is more likely to be precipitated than is lead hydroxide in atmospheres containing CO_2. Formation of the lead basic carbonate species is also predicted from the solubility products which indicate that lead basic carbonate is thermodynamically more stable than the other lead compounds listed in Table II.

From the differences in the infrared spectra in Fig. 3, it is concluded that H_2O_2 is responsible for suppressing the formation of carbonate species. Suppression of carbonate or basic carbonate formation in the precipitate may be tied to the ability of H_2O_2 to form complexes with cationic species. It must, however, also be noted that lead compounds are catalytic in the decomposition of H_2O_2; therefore, the H_2O_2 may play a role in controlling the oxygen equilibrium within the system. A higher content of oxygen within the system may allow the formation of Pb-O bonds instead of carbonate containing bonds. Differences in the colour of the as-precipitated powders prepared with and without H_2O_2 additions tends to support the hypothesis that the H_2O_2 affects the oxygen distribution within the system. The red colour of the powders prepared with the H_2O_2 additions, described earlier, suggests bonding similar to red PbO. Additional work needs to be performed in order to determine how H_2O_2 affects the mechanisms of the precipitation process.

Another difference between the two infrared spectra in Fig. 3 is a shift in the position of the broad absorption peak in the region between 1700 and 3200 (cm^{-1}) wavenumbers. The shift of this absorption peak is probably due to differences in hydrogen bonding within the powders. The effects of H_2O_2 upon suppression of hydroxide formation could not be determined from the spectra since the powders contained adsorbed water which is characterized by the absorption peaks at 3450 and 1650 (cm^{-1}) wavenumbers.

Specific surface areas of the as-precipitated powders exhibit a maximum for the powders prepared with H_2O_2 : $PbTiO_3$ ratios between 1.1 : 1 and 2 : 1 as shown in Fig. 4. Since the H_2O_2 affects the speciation in solution and the species that are precipitated from solution, it is also likely that it influences the nucleation and growth rates of the precipitate particles. The nucleation and growth rates of the precipitate control the precipitate particle size and density which ultimately determines the specific surface area of the powder. Low specific surface areas of the powders prepared with H_2O_2 : $PbTiO_3$ ratios less that 1 : 1 are probably due to the formation of the carbonate species within the precipitate. Low specific surface areas for powders prepared with H_2O_2 : $PbTiO_3$ ratios above 2 : 1 are probably due to changes in the quantity of structural water within the precipitate.

3.4. Effects of pH upon precipitate properties

The as-precipitated powders prepared at the six different pH ranges of 8.00 to 8.20, 8.50 to 8.65, 8.90 to 9.15, 9.65 to 9.75, 9.90 to 10.05 and 10.15 to 10.30 and constant H_2O_2 : $PbTiO_3$ ratio of 1.1 : 1 were analysed by X-ray diffraction. The patterns obtained were similar to those described previously. The precipitates are amorphous, and absence of change in the positions of the broad amorphous peaks indicates that there is little or no change in short range order with changing pH. All the infrared spectra were similar to the bottom spectra in Fig. 3. Infrared absorption spectra recorded between 4000 and 400 (cm^{-1}) wavenumbers also did not exhibit any change as a function of pH.

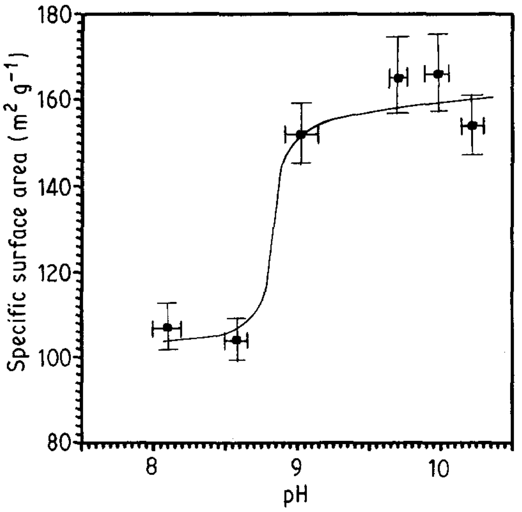

Figure 5 Effects of precipitation pH upon the specific surface area of as-precipitated powders. The large increase in specific surface area occurs where the lead species changes from Pb^{2+} to $HPbO_2^-$.

The specific surface area of the as-precipitated powders measured as a function of pH is shown in Fig. 5. Precipitates prepared below pH 9.00 have lower specific surface areas than those prepared above pH 9.00. The large increase in specific surface area at pH $\approx$ 9.00 occurs at approximately the same pH as the solubility minimum for the lead system (pH = 9.34) indicated by Pourbaix [15]. This finding strongly suggests that the effect of pH upon specific surface area is due to change in speciation of the lead from Pb^{2+} to $HPbO_2^-$. Since one of the lead species is positive and the other negative, the mechanisms for precipitation will also probably differ. Differences in the mechanisms for precipitation would ultimately lead to differences in nucleation and growth rates for the solid precipitate.

4. Conclusions

A study has been made of the influence of H_2O_2 and pH upon the coprecipitation process used in making $PbTiO_3$. Without H_2O_2 additions to the mixed solution used for coprecipitation, dissolved CO_2 in the solution caused the formation of carbonate species in the precipitate. Lead basic carbonate is one of the most thermodynamically stable compounds that can be formed from the coprecipitation method under study. Therefore, formation of carbonate species can be expected for any precipitate prepared under a CO_2 containing atmosphere. However, when H_2O_2 was added to the mixed solution, carbonate formation was suppressed. Suppression of carbonate formation was apparently due to an effect upon the mechanisms for precipitation because of changes in the nature of the complex species present in the precipitating solutions.

Both the pH and the H_2O_2 show a pronounced effect upon the specific surface area of the as-precipitated powders. The H_2O_2 concentration alters the species which are contained in the precipitates and therefore changes the nucleation and growth rates of the precipitate particles. Since the pH controls the aqueous lead complex species present in solution, the pH directly affects the precipitation reaction mechanisms which determine the nucleation and growth rates of the precipitate particles. Both H_2O_2 and pH strongly affect the complex ionic equilibrium for any Pb/Ti coprecipitation process.

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