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Surface Area, XRD, and FTIR Spectral Characterization of Chemically Derived $PbTiO_3$ Ceramics

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The Fourier transform infrared (FTIR) spectroscopic technique has been used to follow the reaction sequence during thermal treatment of the precursor powders of a modified lead titanate composition. The precursor powders were prepared by three different techniques—gel processing, chemical coprecipitation, and attrition milling. X-ray diffraction (XRD) and surface area measurements on powders calcined at various temperatures were also conducted to monitor the structural changes and the thermal reactivity of the powders. The results suggest that FTIR is a relatively simple and more sensitive technique than XRD for the characterization of these powders at various stages of reaction.

Introduction

Lead titanate is a ferroelectric material and belongs to the perovskite family of ceramics along wtih several others such as barium titanate, potassium niobate, and lead zirconate titanate. All these materials are characterized by one or more phase transitions within a given range of temperatures. However, lead titanate is unique because of its high Curie temperature (~490°C), and the highest spontaneous polarization in the tetragonal phase. These features make it attractive for high temperature, high frequency transducer applications. In addition, other features, e.g., the virtual absence of piezoelectric coupling in the transverse mode, low mechanical quality factor Q_m, and low dielectric constant of this material, make it a prime candidate for underwater transducers at low frequency or for high frequency transducers for medical diagnostics and ultrasonic nondestructive testing of materials.

However, pure lead titanate cannot be sintered to give dense ceramic bodies. This is because the large anisotropy in the tetragonal phase (c/a = 1.063) induces large stresses in the material when the sample is cooled after sintering through the cubic-to-tetragonal phase transition. These stresses induce micro- and macro-cracks in the sintered body, and the resulting material is porous, fragile, and too difficult to polarize.

It has been shown (*1–3*) that the above problems in sintering lead titanate can be easily overcome if a portion of the lead and titanium ions are substituted by various metallic ions. In particular, a calcium-modified lead titanate composition introduced by Yamashita *et al.* (*4*), offers a combination of piezoelectric and mechanical properties that

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make it very promising for a variety of transducer applications.

Conventionally, ceramic precursor powders are produced by mechanical mixing (ball milling or attrition milling) of the raw materials in the form of oxides or carbonates. These techniques are plagued with inherent problems—e.g., inhomogeneous mixing, contamination due to grinding of the milling media, large particle size, etc. A powder with a relatively coarse particle size requires higher densification temperatures and the inhomogeneity in the precursor powders often results in the formation of undesired phases in the sintered body which may adversely affect the final properties of the product. The higher sintering temperatures are undesirable especially in the sintering of lead titanate-based ceramics due to the greater evaporation of lead oxide resulting in porous and nonstoichiometric sintered products.

Chemical routes for the processing of ceramic precursor powders offer several advantages, e.g., greater control of chemical composition, homogeneity (as the mixing obtained in solutions is at the molecular scale), less contamination, ultrafine powders, and other parameters necessary to produce high performance ceramics. For example, sol–gel processing has been shown to produce inorganic precursors of enhanced quality (*5–8*).

The final properties of a ceramic body are often highly sensitive to the initial steps used to process the precursor powders. In order to produce a high performance product, it is important to follow the physical and structural changes that occur during initial processing steps. Fourier transform spectroscopy offers a convenient tool to monitor such changes during processing of ceramic precursor powders, especially when chemical routes for synthesis are adopted. This report describes the chemical processing and characterization (using FTIR, XRD, and surface area measurements) of a modified lead titanate composition having the general formula

$$[Pb_{1-x}Ca_x][(Co,W)_yMn_zTi_{1-2y-z}]O_3$$

where $x \geq 0.1$ and ≤ 0.35, $y \geq 0.01$ and ≤ 0.03, $z \geq 0.01$ and ≤ 0.02. Chemical coprecipitation and gel processing techniques were used to synthesize the precursor powders. Powders of the same overall composition were also prepared by a conventional attrition milling method so that the differences in physical properties and structural development as a function of processing temperature for the powders produced via chemical and conventional processing routes could be ascertained.

Experimental Procedures

For gel processing, appropriate amounts of $PbCO_3$, Ca, Co, and Mn acetates were dissolved in 80% aqueous acetic acid. Titantium–*N*–tetrabutoxide (TNBT), also dissolved in 80% aqueous acetic acid, was then added in small drops to the above mixture to give a pink solution. This solution was evaporated in a rotary vacuum flask at ~40°C to form a viscous gel. The gel was subsequently precipitated in isopropanol and splat dried at 125°C to give bluish grey powders.

For chemical coprecipitation, Pb, Ca, Co, and Mn acetates were dissolved in a small amount of water at ~60°C. TNBT was dissolved in excess oxalic acid, forming a yellow solution which was then added in small drops to the acetates to form pinkish precipitates. The precipitation was completed by adding concentrated ammonium hydroxide to a pH of 8.5. The mixture was evaporated in a rotary vacuum flask and oven dried at 125°C.

The conventional approach involved wet attrition milling of the raw materials in the form of oxides or carbonates for 4 hr followed by vacuum filtration of the slurry and subsequent oven drying at 125°C. Details of

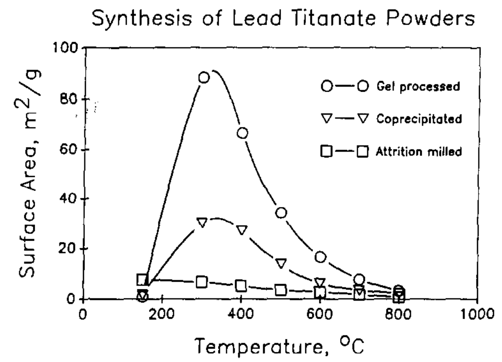

FIG. 1. Calcination temperature dependence of the surface area of gel-derived, coprecipitated, and attrition-milled powders.

the powder synthesis are given elsewhere (*9*).

Powders were calcined in small batches (<10 g) in alumina crucibles loosely covered with platinum foil at temperatures ranging from 150 to 800°C. The samples were kept at the desired temperature for a period of 2hr and allowed to cool down to room temperature by turning off the furnace. X-ray diffraction patterns for these powders were obtained using a Rigaku automated powder diffractometer with Cu*K*α radiation and a graphite monochromator. The surface areas were measured by the BET method using a Quantasorb Model QS-10 surface area analyzer. A Digilab Model FTS40, FTIR spectrophotometer was used to obtain IR spectra of solids using lightly loaded (<1%) KRr-supported disks. FTIR spectra of liquids were measured using AgCl cells.

Results and Discussion

Surface Area and XRD Studies

The surface areas of the powders displayed strong dependence both on the method of synthesis and on the calcination temperatures (Fig. 1). At the lower calcination temperatures, the surface areas of the chemically derived powders were slightly lower than those of the powders produced by conventional attrition milling. However, the surface areas of the chemically derived powders increased significantly with the increase in calcination temperatures, due presumably to the formation of the lower density intermediate products by thermal reaction. The gel-derived and coprecipitated powders exhibited the highest surface areas (~90 m^2/g and 30 m^2/g, respectively) at 300°C. Further heat treatment of the powders resulted in a reduction of the surface areas due to crystal growth and partial densification of the particles. After calcination at 600°C, the surface areas of the chemically derived powders were two to five times greater than powders produced via the attrition milling method.

The phase development as evidenced from XRD patterns also showed strong dependence on the powder preparation methods and the calcination temperatures. The gel-derived material was predominantly amorphous up to 400°C. At 500°C, the lead titanate phase was well developed in all three powders along with PbO, TiO_2, and

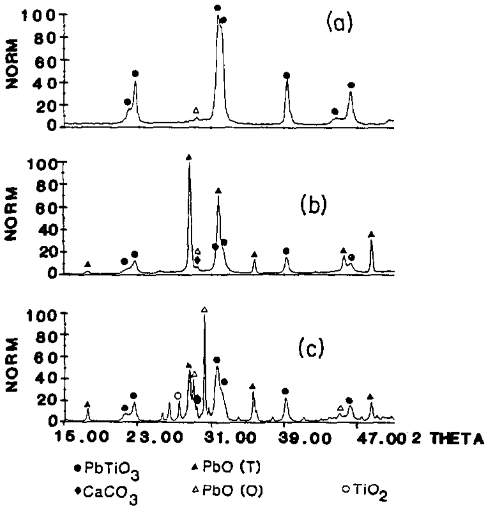

FIG. 2. X-ray diffraction patterns of (a) gel-derived, (b) coprecipitated, and (c) attrition-milled powders calcined at 500°C.

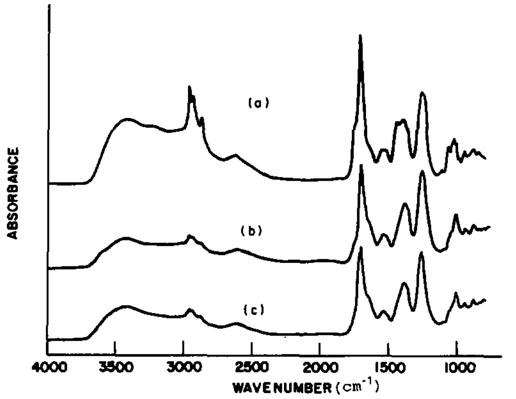

FIG. 3. FTIR spectra of TNBT (a), TNBT + $PbCO_3$ (b), and TNBT + $PbCO_3$ + $CaCO_3$ (c), in acetic acid solution at room temperature.

$CaCO_3$ present as undesired phases (Fig. 2). Above 600°C, gel-derived material produced single phase lead titanate; however, both coprecipitated and attrition-milled materials continued to display trace amounts of impurity phases even after heat treatment to ~800°C. Details of the X-ray diffraction studies are given elsewhere (*9*).

FTIR Studies

The FTIR spectra of the major components, e.g., TNBT, TNBT + $PbCO_3$, and TNBT + $PbCO_3$ + $CaCO_3$ in acetic acid as well as oxalic acid solutions were recorded to provide the basis for identifying the reaction pathways during gel processing and chemical coprecipitation. Figure 3 shows the solution FTIR spectra of these components in aqueous acetic acids. It is evident that the three spectra are dominated by the acetate ions. The broad absorption bands around 3400 cm^{-1} are due to stretching vibrations of the —O—O—H, hydrogen bonds. The multiple bands around 2900 cm^{-1} could be assigned to the stretching vibrations of the acetate ions. The rather broad peak at around 2600 cm^{-1} is presumably the combination band for the acetate ions. This assignment is compatible with the corresponding assignment for the sodium acetate ions made by Ito *et al.* (*10*). The strong band around 1700 cm^{-1} is typical of the C═O stretching vibration of the acetic acid that normally exists as a dimer. The carboxylate ion (COO) asymmetric stretch vibrations O—C—O appear around 1500 cm^{-1}. A shoulder band around 1350 cm^{-1} is due to the CH_3 deformation vibrations. Similar assignments have been previously reported for the other acetate complexes (*10, 11*). The intense peak around 1270 cm^{-1} is characteristic of the C–O stretching vibration of the carboxylic acid dimer. The bands around 1050–1100 cm^{-1} are due to the CH_3-C rocking vibration. The peaks between 850 and 1050 cm^{-1} cannot be assigned to C–C stretching vibrations, since in acetates these vibrations are not infrared active (*12*). These bands could be due to the metal–acetate bonding and O–H deformation vibrations.

The powder FTIR spectra of the intended composition processed by the gel technique and calcined at temperatures ranging from 150 to 800°C are shown in Fig. 4. Heat treatment of the dried powder (obtained via rotary evaporation of the solution) at 150°C resulted in the reduction of relative band intensities corresponding to O–H, C–H, C═O, and C–O stretching vibrations (at

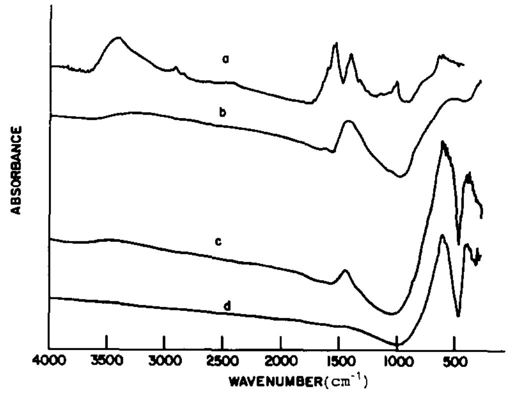

FIG. 4. FTIR spectra of gel-derived powders heat treated to (a) 150°C, (b) 300°C, (c) 600°C, and (d) 800°C.

3400, 2900, 1700, and 1270 cm^{-1}, respectively) due to the partial loss of water and acetic acid from the material. The loss of acid/water also improved the resolution of the remaining peaks in the 1000- to 1600-cm^{-1} region. The broad band near 800 cm^{-1} is typical of metal–oxygen bonding and the peak centered around 625 cm^{-1} could be due to COO out-of-plane rocking vibration. The bands in the 400- to 600-cm^{-1} region are probably due to various skeletal and COO in-plane vibrations.

Heat treatment of the gel-derived powders at 300°C resulted in almost complete disappearance of the peaks corresponding to C–H, C=O, C–O, and COO functional groups, indicating the decomposition of organic materials. The band around 1450 cm^{-1} could be a combination of carbonyl absorption due to metal carbonate and residual carboxylate ion. DTA studies (*13*) also support the formation of carbonates at this temperature. The broad absorption bands in the 300- to 600-cm^{-1} region are due to metal–oxygen bonding. It is interesting that the hydroxyl group peaks (at ~3400 and 1600 cm^{-1}, respectively) still exist in powders dried at 300°C. This could be due to the moisture absorption by particles having very high surface area as discussed in the previous section. At 600°C the carbonate ion peak at ~1450 cm^{-1} is significantly reduced in intensity and the metal–oxygen peak at ~400 and 600 cm^{-1} characteristic of lead titanate material (*14*) are quite apparent. At 800°C the carbonate ion peak (~1450 cm^{-1}) disappears indicating the complete decomposition of carbonates into oxides and the subsequent formation of $PbTiO_3$-based product. Only well-resolved lead titanate peaks are present at this temperature, suggesting the formation of single phase material.

The FTIR spectra of TNBT, TNBT + lead acetate, and TNBT + lead acetate + calcium carbonate, coprecipitated as oxalates/hydroxides and dried at 35°C, are shown in Fig. 5. It is clear that these spectra are primarily dominated by oxalate ions. The broad absorption bands between 2500 and 3500 cm^{-1} are due to the stretching vibrations of the N–H and O–H groups as previously reported for the titanyl–oxalate system (*15, 16*) prepared from ammoniacal solutions. The other broad absorption band around 1800–2200 cm^{-1} could be assigned to carboxylate amino acids or amino acid salts. The intense bands around the 1590- to 1700-cm^{-1} region are due the asymmetric stretching vibrations of the oxalate (C=O) group. The barium and ammonium salts of the oxalates exhibit similar spectra and are typical for complexes with bidentate and bridging oxalate groups (*17, 18*). The peak splitting for this band could be related to the formation of various di- or trioxalate–metal complexes (*19*). The bands arising from deformation vibration of water or hydrated complexes are not visible as they overlap with the asymmetric vibration of the oxalate group at ~1600 cm^{-1} and are probably hidden under this band. The band centered around 1425 cm^{-1} could be assigned to the coupled stretching vibrations due to C–O + C–C groups and also partially due to the NH_4 ion band that occurs in the same region (*17, 20*). The absorption band in the 1275-

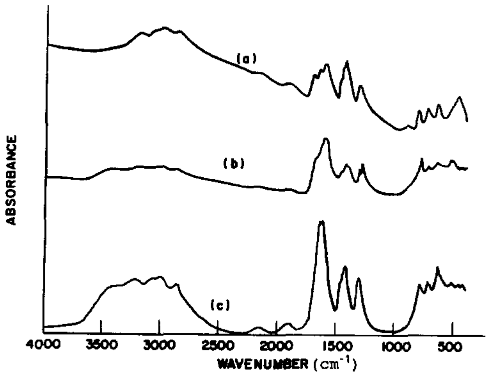

FIG. 5. FTIR spectra of TNBT (a), TNBT + lead acetate (b), and TNBT + lead acetate + calcium carbonate coprecipitated as oxalate/hydroxide and dried at 35°C.

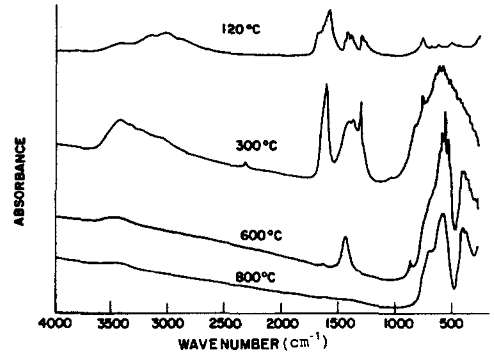

FIG. 6. FTIR spectra of coprecipitated powders calcined at 120°C, 300°C, 600°C, and 800°C.

to 1325-cm^{-1} region could be due to either the stretching vibration of the COO group (*18*) or the coupled vibrations of the symmetric stretch of the C–O and in-plane O–C=O groups (*20*). The bands between 650 and 900 cm^{-1} could be due to coupled vibrations of the various functional groups, e.g., C–O and metal–oxygen (*M*—O) stretching and O–C=O in-plane deformation vibrations. The bands between 400 and 650 cm^{-1} are probably due to various ring deformations, metal–oxygen bonding, and combination vibrations of the oxalate, amino-oxalate, and hydroxyl groups.

The FTIR spectra of the powders of the given composition prepared by coprecipitation and dried at temperatures ranging from 150 to 800°C are given in Fig. 6. The spectral features of the powders dried at 150°C are similar to those produced at 35°C (i.e., dominated by oxalate ion). However, the spectral resolution seems to have improved due to the loss of water by heat treatment. Powders dried at 300°C exhibit relatively increased peak intensity at ~1425 cm^{-1}, possibly due to the formation of carbonates as a result of decomposition of organics. This spectrum also shows some depletion of oxalate in general as well as enhancement in the metal–oxygen bonding peak intensity centered around 600 cm^{-1}. The weak, sharp peak around 2330 cm^{-1} has been interpreted in the literature as being due to retained carbon dioxide (*18*). The spectrum also displays increased band intensity of O–H groups due to increased moisture absorption by the ultrafine particles produced at this temperature. The coprecipitated powders also displayed the highest surface area at this temperature. At 600°C, the metal–carbonate peaks at ~1450 and 800 cm^{-1} and the metal–oxygen peaks at ~400 and 600 cm^{-1} (due to lead titanate formation) are clearly observed. The XRD data also indicate $PbTiO_3$ formation at this temperature. Heat treatment at 800°C results in the disappearance of the carbonate peaks due to the decomposition of carbonates into oxides and the formation of the lead titanate product. The lead titanate peaks are now more clearly resolved. The weak absorption band around 3400 cm^{-1} is proabably due to the moisture absorption from the environment.

Figure 7 depicts the FTIR spectra of powders of the modified $PbTiO_3$ composition prepared by attrition milling the raw materials and heat treating at temperatures ranging from 300 to 800°C. At 300°C the spectrum exhibits a broad hydroxyl group band around ~3450 cm^{-1} apparently due to the

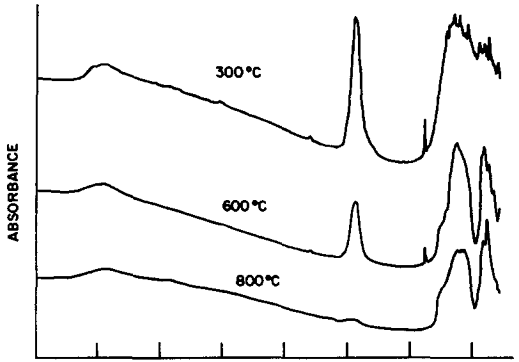

FIG. 7. FTIR spectra of modified lead titanate composition prepared by attrition-milling process and calcined at 300°C, 600°C, and 800°C.

moisture absorption by the powder. Other features of the spectrum include two sharp peaks at ~1430 and 875 cm^{-1}, respectively, indicating the presence of carbonate anions and two rather broad peaks centered around 400 and 625 cm^{-1} due to the metal–oxygen bonding complexes in the product. It should be noted that the raw materials for the intended composition included $CaCO_3$, $CoCO_3$, and $MnCO_3$ as minor components. This may explain the presence of the observed carbonate ion peaks in the spectrum. Heat treatment to 600°C resulted in the decomposition of carbonates as evidenced from the reduction in their relative peak intensities; the metal–oxygen bonding peaks (due to the $PbTiO_3$ formation) are well resolved at this temperature. The XRD data also support partial lead titanate formation at this temperature. FTIR spectrum of the powders heat treated to 800°C clearly displayed the $PbTiO_3$ peaks centered around 400 and 600 cm^{-1}. Only trace amounts of carbonates were detectable at this temperature.

Conclusions

The results from the above studies indicate that the materials produced through chemical processing techniques can provide highly reactive ultrafine powders upon calcination. The surface area studies show that among the three powder processing methods, the gel process provides the most reactive powders. This is further supported through XRD data which indicate the gel material to be virtually free of impurity phases (single phase $PbTiO_3$) when heat-treated at 600°C. The powders produced via coprecipitation and attrition milling methods contained impurity phases even when heat-treated to 800°C. The FTIR studies however indicated the presence of residual carbonates in gel-derived materials calcined at 600°C, suggesting FTIR spectroscopy to be a more sensitive technique than XRD at least in some cases. The FTIR spectra also indicated that at lower temperatures, both gel-derived and coprecipitated materials are dominated by the presence of acetate and oxalate ions, respectively. At 300°C, both materials showed the presence of carbonates due to the decomposition of organics. At 600°C, the partial decomposition of carbonates and subsequent $PbTiO_3$ phase formation occurred. Only gel-derived materials produced single phase $PbTiO_3$ when heat treated to 800°C. Thus gel processing appears to be the most favorable route for the preparation of the modified lead titanate composition.

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