Polymeric citrate precursor route to the synthesis of nano-sized barium lead titanates

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Abstract

Monophasic oxides of the formula, Ba$_{1-x}$Pb$_x$TiO$_3$ (0 < x < 1) were obtained at temperatures close to 500 °C from polymeric precursors formed using citric acid and ethylene glycol. These oxides were found to be tetragonal for all values of x, the distortion increasing with Pb content. Differential scanning calorimetry (DSC) shows that the decomposition of the precursor to the oxides varies with composition and the decomposition temperature is highest (530 °C) for the x = 0.5 composition. X-ray line broadening studies of 900 °C sintered samples show grain size of 50-54 nm in all compositions. TEM studies show agglomerated grains of the size, 40-60 nm. The dielectric constant (e) decreases with lead-doping having a value 70 for PbTiO$_3$. The dielectric loss (D) for different compositions varied between 0.005 and 0.01 at 100 kHz. The dielectric constant and loss show excellent frequency stability.

Keywords: Oxides; Chemical synthesis; X-ray diffraction; Dielectric properties

1. Introduction

Lead titanate is an excellent ferroelectric having the highest Curie temperature known among perovskite-type oxides. Almost any substitution of lead with suitable ions (Ba, Sr or Ca) which are likely to form a perovskite-type lattice causes a lowering of the Curie temperature. Barium titanate and its related compounds have been extensively used in the preparation of high dielectric constant capacitors, PTC resistors, transducers and ferroelectric memories [1].

Due to the tremendous technological applications of both the above oxides attempts are constantly being made to get improved properties by obtaining finer particles. BaTiO$_3$ has been synthesized earlier by several methods including chemical precipitation [2,3], sol-gel [4] and hydrothermal methods [5] and metal-organic precursors [6]. PbTiO$_3$ has also been synthesized as a fine powder by the
coprecipitation [7], sol-gel [4,8] and hydrothermal methods [9]. The oxalate method [10] is known to give a stoichiometric precursor of the oxide (BaTiO$_3$ or PbTiO$_3$). Saegusa et al. [11] have prepared high purity stoichiometric fine particles of lead barium titanate from lead barium titanyl oxalate prepared from ammonium oxalate, oxalic acid and barium acetate.

Although there have been several earlier investigations on the preparation of dielectric oxides like BaTiO$_3$, SrTiO$_3$, PbTiO$_3$, etc. by chemical routes to obtain homogeneous, monophasic fine-grained oxides, there has been very little effort to study and characterize the detailed dielectric properties. Most of the reports [5-13] discuss only the synthesis and structural aspects and grain sizes with little or no correlation with dielectric properties. In today's world of thin-layer dielectrics it is of significance to understand the effect of reducing grain sizes on the dielectric properties. It is also found that most of the studies carried out on fine powder synthesis of dielectric oxides seldom discuss about the grains size, structural aspects and other related aspects of the sintered materials obtained from the fine powders. The characterization of these sintered ceramics is of vital importance for judging the suitability of the ceramic in applications. Some studies [14-17] on BaTiO$_3$ show that there is a tetragonal to cubic transition with decrease in grain size. A detailed study [18] on barium strontium titanates discusses some of the properties of sintered ceramics obtained from fine particles.

In this paper we report the synthesis of barium lead titanates, Ba$_{1-x}$Pb$_x$TiO$_3$ ($0.25 \leq x \leq 1.0$) by the polymerized citrate method based on the Pechini type reaction route [19]. The polymeric citrate precursor route has been used earlier by Arima et al. [20] for the synthesis of BaTiO$_3$ fine particles. Oxides of the type, Ba$_{1-x}$Sr$_x$TiO$_3$ have also been prepared earlier [18] by the above method to yield nano-sized grains of around 30-50 nm diameter. The success of the above synthesis encouraged us to use the citrate precursor route to obtained the Ba$_{1-x}$Pb$_x$TiO$_3$ oxides. The oxides obtained by us have been analyzed by chemical and spectrophotometric methods to ascertain the stoichiometry. We have carried out detailed X-ray diffraction (XRD), thermal (TGA, DSC) and FT-IR studies of the gel and precursors obtained by the citrate method. In addition, we report the powder XRD, differential scanning calorimetry (DSC) and detailed dielectric properties of the barium lead titanates sintered at 900 $^\circ$C. The dielectric properties were studied in the frequency range of 50 Hz to 500 kHz.

Our main aim is to synthesize homogeneous nano-sized barium lead titanates and to understand the effect of decreasing grain size on the dielectric properties of these oxides. Such information would be useful to device manufacturers especially those involved with thin-layer dielectrics.

2. Experimental

Three millilitres of titanium tetraisopropoxide (Acros 98%+) was added to 22.5 ml of ethylene glycol (Qualigens SQ grade) under nitrogen atmosphere. The mixture was stirred on a magnetic stirrer for 10 min to get a clear transparent solution. To this solution 19.2 g of dried citric acid (Qualigens SQ grade, 99.5%) was added. A whitish precipitate was observed immediately after adding citric acid to the solution but it dissolved after stirring the solution for 4-5 min. The contents were stirred at room temperature till a clear, viscous solution was obtained.

Barium carbonate (Loba Chemie, GR grade 99%) and lead nitrate (Fluka) were dried in an oven at 110 $^\circ$C for 2 h and ground to powder. Stoichiometric amounts of the carbonate and nitrate were weighed and added to the ethylene glycol-citric acid-Ti-isopropoxide solution prepared as above. The contents were stirred on a magnetic stirrer till the carbonates dissolve and we get a clear transparent solution. The
solution was then kept in an oven at 135 ± 5 °C for 20 h to evaporate the solvent and to promote polymerization. The solution changes to a dark viscous resin. This resin was kept in an electrical heated furnace for 2 h at 300 °C for charring and then cooled to room temperature. The resin turns to a black mass, which was ground to a powder in an agate mortar. This ground black mass is henceforth called a precursor. Barium lead titanate powders were obtained by heating this precursor at 500 °C for 20 h and then at 800 °C for 8 h. This was obtained as a white powder. The product was compacted into pellets (with few drops of 5% polyvinylalcohol solution) at a pressure of 4 t and then sintered at 900 °C for 12 h.

Barium and lead content of Baj PbTiOs (x = 0-1.0) was estimated as BaSO₄ and PbSO₄ and determined as sum of barium and lead sulfates in BaxPb₃TiO₃ powders.

Wet chemical analysis was carried out for all barium lead titanate powders calcined at 800 °C for 8 h. The filtrate obtained in the above analysis was used for titanium estimation. Acidic titanium (IV) solution gives a yellow colour with hydrogen peroxide. The intensity of the color depends on the concentration of titanium. The filtrate obtained above was transferred to a 100 ml volumetric flask and made up to the mark with distilled water. Standard solutions containing 10, 20, 30 and 40 ppm concentration were made by dissolving TiO₂ (99.99%, CDH) in concentrated sulfuric acid, and then diluting with distilled water. Twenty millilitres of each sample was taken in 50 ml volumetric flask and 5 ml of 3% H₂O₂ was added to it and the volume was made up to the mark. Absorbance of the standard and sample solutions was measured using UV-Vis spectrophotometer GS 5701V (ECIL make) at λmax of 410 nm. A calibration graph of concentration versus absorbance was plotted for the standard solutions and the concentration of the sample solution was evaluated from the calibration curve. Chemical analysis

![Fig. 1. Powder XRD patterns for (a) PbTiO₃ precursor obtained after heating at 300 °C for 2 h and (b) PbTiO₃ obtained after heating the precursor at 500 °C for 20 h.](image-url)
of the barium lead titanate powders shows excellent agreement between the theoretical and observed values as given in Table 1. We have checked for the possibility of metallic lead being obtained during the calcination and sintering (since organic compounds are being used in the synthesis). The oxide obtained after heating at 900 °C was kept overnight in concentrated HNO₃ (lead should dissolve) and the Pb-content in the filtrate was estimated using a Perkin-Elmer Atomic Absorption Spectrophotometer (model Analyst 100). We found a very insignificant amount (less than 3%) of lead in the solution which may be also due to slow dissolution of the lead titanium oxide. Note that the powder XRD studies showed no reflection due to lead (both before and after adding the oxide to concentrated HNO₃).

Fig. 2. XRD patterns for oxides of Ba₁₋ₓPbₓTiO₃ system sintered at 900 °C for 12 h. Inset shows XRD pattern (slow scan) showing weak tetragonal distortion in the x = 0.25 composition.
Table 1
Results of the chemical analysis of barium lead titanates

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>Experimental value</th>
<th>Calculated value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% Ti</td>
<td>% Pb + Ba</td>
</tr>
<tr>
<td>Ba_{0.35}Pb_{0.65}TiO_{3}</td>
<td>19.20</td>
<td>60.71</td>
</tr>
<tr>
<td>Ba_{0.5}Pb_{0.5}TiO_{3}</td>
<td>18.20</td>
<td>62.24</td>
</tr>
<tr>
<td>Ba_{0.75}Pb_{0.25}TiO_{3}</td>
<td>17.06</td>
<td>65.45</td>
</tr>
<tr>
<td>PbTiO_{3}</td>
<td>14.36</td>
<td>67.16</td>
</tr>
</tbody>
</table>

The barium lead titanate powders were characterized by powder XRD using a Bruker D8 Advance X-ray diffractometer with Ni-filtered Cu Ka radiation. Scan rates of 2 deg/min were used for normal scans. For careful X-ray studies slow scans with step size of 0.0058 in 2θ and step-time of 2 s was employed. In addition the Ka2 stripping procedure was used. To obtain the grain size from X-ray line broadening, the Scherer’s formula \( t = \frac{0.9d}{B \cos \gamma} \) was applied where ‘t’ is the diameter of the grain, \( d \) is the wavelength (Cu Ka1; Ka2 was stripped off), \( B^2 = B_{M}^2 - B_{S}^2 \) where \( B_{M} \) is the full-width at half maximum of the sample and \( B_{S} \) is that of a standard of grain size of around 2 mm. The standard (Quartz, sintered) was so chosen such that the peak (whose width is to be measured) of the sample and the standard are having similar 2θ values. The (1 1 1) reflection of the observed X-ray data was chosen for calculating the grain size of the barium lead titanate oxides. The grain size was also determined from transmission electron microscopy using a JEOL 200 CX electron microscope operating at 120 kV. The FT-IR spectra were taken on a Nicolet 460 Protégé spectrophotometer in the range from 4000 to 225 cm\(^{-1}\) after every step in the synthesis till 800 °C. FT-IR spectra of barium lead titanate gel were recorded on CsBr disk and the calcined powders and precursor on KBr disk. Thermogravimetric analysis (TGA) and DSC of precursors were recorded on Netzsch Simultaneous Thermal Analyzer.

![Graph](image-url)

Fig. 3. Plot of the variation of the (a) lattice parameters and (b) the \( da \) parameter with composition ‘x’ in Ba_{1-x}Pb_xTiO_3.
Model 409 EP, with heating rate 10 °C/min in air. Dielectric properties were measured on sintered disks coated with silver paste (dried at 90 °C for 6 h) using a Hewlett-Packard multi-frequency LCR meter (HP 4284L) in the frequency range from 50 Hz to 500 kHz. The density of the sintered disks were obtained by the Archimedes method using CCl₄. The disks were soaked in the organic medium for sufficiently long time and weights were taken till a constant weight was observed. For consistency three different density measurements were carried out for each sample. The density was found to vary between 93 and 94% of theoretical density.

3. Results and discussion

Oxides of the type, BajPbTio₃, were obtained after heating the precursors (see Section 2) at 500 °C. These powders retained the monophasic nature on further heating and sintering. The gel formed

![FT-IR spectra](image)

Fig. 4. FT-IR spectra of the x — 0.5 composition of Ba1-xPb_xTIO_3 after various heat treatments. (a) Polymeric gel heated at 135 °C, (b) after heating at 300 °C (c) after heating at 500 °C, and (d) after heating at 800 °C.
(after 135 °C) and the precursor (after 300 °C) heating showed amorphous nature as observed from the powder XRD studies. Further heating of the powders around 500 °C led to the formation of the pure oxides (Fig. 1).

The powder XRD patterns could be indexed on the basis of a tetragonal cell (Fig. 2). The plot of lattice parameters (Fig. 3(a)) show that the a-parameter decreases while the c-parameter increases with increase in Pb-content. The da parameter increases (Fig. 3(b)) with Pb-content indicating the increase in the tetragonal distortion. Note that the x = 0 and 0.25 compositions show very weak tetragonal distortion and could be observed only by careful X-ray analysis (slow scan with 0.0058 step size with step-time of 2 s and with Ka2 stripping) of the 900 °C sintered samples. The two reflections (2 0 0) and (0 0 2) overlap partially to give an asymmetric peak (inset of Fig. 2).

FT-IR studies of various compositions of lead doped barium titanate have been obtained after each step of the synthesis. In Figs. 4 and 5, the IR spectra of the compounds with x = 0.5 and 1.0 have been

![Fig. 5. FT-IR spectra of the x = 1.0 composition of Ba\(_x\)Pb\(_{1-x}\)TiO\(_3\) after various heat treatments. (a) Polymeric gel heated at 135 °C, (b) after heating at 300 °C, (c) after heating at 500 °C and (d) after heating at 800 °C.](image-url)
shown. In the case of the polymeric gel heated at 135 °C, we find IR bands for OH stretch, carboxylate anion, the ester band and the carbonate species (Figs. 4(a) and 5(a)). On further heating at 300 °C to form the precursor we find the disappearance of the OH band (Fig. 5(b)). However, we find a broad peak pertaining to adsorbed water. The carboxylate and carbonate bands are present at this temperature. After heating the sample at 500 °C (Fig. 4(c)), the carbonate band is present, which disappears at 800 °C (Fig. 4(d)). However, in PbTiO$_3$ ($x = 1$) the carbonate band is absent after the 500 °C heating as seen in Fig. 5(c). The broad Ti-O bands (as normally observed in BaTiO$_3$) in the region, 270-400 and 585-700 cm$^{-1}$, are clearly visible in the 500 °C heated sample (Figs. 4(c) and 5(c)).

We have also carried out the TGA of the precursors as shown in Fig. 6(i). It is seen that the temperature at which the decomposition of the precursor begins varies with composition, and increases from 250 °C for the $x = 0$ composition to 300 °C for the $x = 1$ composition. The decompositions are complete at temperatures ranging from 580 to 600 °C depending on the composition. This explains the presence of the CO$_3^{2-}$ band in the IR of the sample heated at 500 °C (Fig. 5(c)).

The differential scanning calorimetric (DSC) studies of the precursors of the BPT materials are shown in Fig. 6(ii). The decomposition is accompanied by the presence of an exothermic peak. The decomposition temperature initially increases with increasing lead content between the $x$ values of 0-0.25, from 465 to 527 °C (see inset of Fig. 6(ii)). However, it falls of sharply at high lead content.

![Fig. 6](image)

Fig. 6. (i) Thermogravimetric (TGA) plots and (ii) DSC plots of Ba$_{1-x}$Pb$_x$TiO$_3$ at (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1.0$. Inset shows the variation of the decomposition temperature of the precursor with composition.
A careful look at the DSC curves reveals an asymmetry of the exotherms in some of the compositions, which indicate that there are two close decomposition temperatures.

Rationalizing the XRD, IR and DSC data we can then say that there may be decomposition of the carbonates starting from around 250 to 300 °C and completing around 480 to 550 °C depending on the composition. So around 500 °C there may be some amorphous metal carbonates present in the x = 0.5 composition (as the carbonate band is observed in IR studies, Fig. 4(c)) which are not observed in the XRD. It may be noted that an earlier study on PBT fine particles was reported [21] using the decomposition of lead barium titanyl oxalate precursor, PbₙBa₁₋ₓTiO(C₂O₄)₂·4H₂O, where these precursors had much higher decomposition temperatures ranging from 630 to 700 °C.

Apart from the powder XRD studies carried out for structural characterization (discussed earlier), we have also carried out detailed line broadening studies using XRD to evaluate the grain size of the barium lead titanates. The grain size of the 900 °C sintered samples were calculated from X-ray studies.

![Fig. 7. Transmission electron micrograph (TEM) of (a) Ba₀.5Pb₀.5TiO₃ and (b) PbTiO₃.](image-url)
using the Scherer's formula (see Section 2 for details). The average grain size was calculated to be around 54 nm for Ba$_{0.75}$Pb$_{0.25}$TiO$_3$ and 50 nm for PbTiO$_3$. We have also carried TEM studies of some of the above oxides. These studies show particles in the range of 40-60 nm (Fig. 7) which corroborate well with the X-ray line broadening studies.

We have studied the dielectric constant and the dielectric loss of the sintered disks of barium lead titanates as a function of frequency. In Fig. 8, we show the variation of the dielectric constant as a

![Graph](image-url)

Fig. 8. Variation of the dielectric constant ($\varepsilon$) and dielectric loss ($D$) with frequency for Ba$_{1-x}$Pb$_x$TiO$_3$ system. (a) $x = 0.25$, (b) $x = 0.50$, (c) $x = 0.75$, and (d) $x = 1.00$. 

function of frequency measured at room temperature. The dielectric constant for BaTiO₃ prepared by the citrate precursor route is found to be 430 at 100 kHz [18] and decreases drastically on lead substitution. All the lead-doped phases show dielectric constant in the region 30-80 at 100 kHz. These Pb-doped barium titanate samples were sintered at 900 °C and the density of these disks was 93-94%. BaTiO₃ prepared by the above method [18] was sintered at 1100 °C and had a density of 95%. Earlier report on BaTiO₃ prepared by sol-gel [4] method show a dielectric constant of 500-650 and 700-900 (at 1 MHz) for samples sintered at 1200 and 1300 °C (for 30 min) respectively. Another report on BaTiO₃ prepared by the oxalate precursor route [21] gave a dielectric constant of 1620 for BaTiO₃. Thus, it appears that the method of synthesis and sintering temperature affect the dielectric constant to a great extent. The dielectric loss for the barium lead titanates also shows nearly constant values till 400 kHz beyond which it shows a small rise. The dielectric loss in this range of frequencies for different compositions is found to vary between 0.005 and 0.10. The dielectric constant shows negligible variation with frequency (10-500 kHz).

The above studies show that we have a family of nano-structured Ba₃₋ₓPbₓTiC phases with nearly constant value of the dielectric constant and dielectric loss over a large range of frequencies (upto 500 kHz) and may have applications as stable dielectrics. Though the dielectric constant is much smaller compared to the ferroelectric phases, the value is sufficiently large for several capacitor applications. These values (60-80) of dielectric constant are large for linear dielectrics and since the loss is quite low (0.005) their dielectric properties may also be investigated in the microwave region. It is also envisaged that such nano-structured materials if required may act as substrates of the ferroelectric analogues and the lattice match would be ideal for epitaxial growth.

4. Conclusions

We have shown the possibility of obtaining monophasic, nano-sized oxides for the entire range of compositions of the type, Ba₃₋ₓPbₓTiO₃ at low temperatures (~500 °C) using the polymeric citrate precursor route. The phases are tetragonal and the distortion increases with 'Pb' content. These materials have grain sizes ranging from 50 to 54 nm. Oxides sintered at 900 °C show appreciable dielectric constant (60-80) and a low loss (0.005) at room temperature. The negligible variation of the dielectric constant with respect to frequency envisages useful applications.

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