Synthesis of active PZT powders via molecular precursor route

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The reactions of sodium zirconyl oxalate, potassium titanyl oxalate and lead nitrate in their stoichiometric ratios at room temperature (298°K) precipitate a molecular precursor, viz., lead zirconyl titanyl oxalate (PZTO). The controlled pyrolysis of PZTO for 6h at 500°C in air resulted in crystalline submicronic powders of lead zirconate titanate (PZT). This method is simple and economical in comparison to the complex precursors derived from the hydrolysis and polycondensation of metal alkoxides.

Lead zirconate titanate (PZT) ceramics with Zr/Ti ratio of 52.5/47.5 are very widely used in piezoelectric transducer applications in recent years, research activities are being increasingly focussed on the synthesis of cost-effective molecular precursors for generation of monophasic, homogeneous and sinteractive PZT powders. As molecular precursors, various metal alkoxides have been used under varying experimental conditions to obtain powders. These are (i) refluxing conditions, (ii) solvent/alkoxide ratio, (iii) alkoxide/water ratio, (iv) solvent species, (v) metal ion distribution in the hydrolysis products, (vi) solubility of various polymeric species and pH. To overcome these difficulties, an attempt is made to generate a molecular precursor, namely, lead zirconyl titanyl oxalate (PZTO) with Zr/Ti = 52.5/47.5 utilizing chemical reactions in solutions of their respective inorganic salts at room temperature. The controlled pyrolysis of PZTO in air resulted in submicronic PZT powders at as low temperature as T ≈ 500°C for 6h. In this paper, we report the synthesis of active PZT powders and their characterization using wet-chemical analysis, XRD, DTA/TG/DTG and IR techniques.

Materials and Methods

Synthesis of PZTO

Sodium oxalate (14.07 g) was dissolved in distilled water to get a solution of pH = 10.1. To this was added an aqueous solution of zirconyl nitrate (15.29 g, pH = 1.2) which resulted in an intermediate precursor solution with pH = 4.3. This was possible due to dissolution of gelateneous precipitate of ZrOC₂O₄ formed instantaneously during mixing of two solutions. Then, an aqueous solution containing potassium titanyl oxalate (16.82 g, pH = 3.1) was added to the above mentioned intermediate precursor solution to obtain a 'clear solution' labeled as A (pH = 4.3), which contained zirconium and titanium in required stoichiometry in the form of a soluble species. The solution (pH = 3.3 labeled as "B") containing lead nitrate (33.12 g) was added to solution A to precipitate a complex precursor with all the three cations. After complete precipitation, the pH was found to be in the range of 2.8-3.1. The precipitate was allowed to settle and the clear supernatant solution was tested for Pb, Zr and Ti cations by usual wet chemical methods. The tests were negative indicating thereby their complete precipitation. The precipitate was finally washed several times with distilled water to avoid contamination of sodium and potassium and filtered using Bückner assembly under vacuum and later air-dried at room temperature.

The as-dried precipitate of PZTO was characterized by chemical analysis, DTA/TG/DTG, XRD and IR techniques. For chemical analysis of (Zr + Ti), a well established procedure of complexing with cupferron in acidic medium was followed. The standard procedure of titration with permanganate solution was followed for estimation of oxalate. Lead was estimated as PbO indirectly by subtracting the weight of (ZrO₂ + TiO₂) from the weight of PZT formed by calcination of PZTO at 800°C for 6h in air. The water content was determined by standard microanalysis techn-
The powder X-ray diffractograms were recorded using Philips PW1730 diffractometer with CuKα radiation (λ=1.5403 Å). Simultaneous DTA/TG/DTG plots were recorded as a function of temperature in air using a Netzsch STA 409 analyser to understand the thermal decomposition behaviour and also to locate the reaction temperature. Transmission electron microscope (JEOL 1200 EX) was employed to study morphology of the PZT powder.

**Results and Discussion**

It is known that both titanium\textsuperscript{13-15} and zirconium\textsuperscript{14-15} form various complex anionic species in acidic medium in the presence of oxalate ions, the concentration of which depends on their pH values. For example, various fractions of species Ti(OH)(C\textsubscript{2}O\textsubscript{4})\textsuperscript{3-}, Ti(OH)\textsubscript{2}(C\textsubscript{2}O\textsubscript{4})\textsuperscript{2-},[TiO(OH)\textsubscript{2}(C\textsubscript{2}O\textsubscript{4})\textsuperscript{3-}] and Ti(OH)\textsubscript{4} are known to form\textsuperscript{15,16} and their concentration is found to change appreciably in the pH range 2-5. Similarly, zirconium is also known to form various anionic species\textsuperscript{16,17} such as ZrO(C\textsubscript{2}O\textsubscript{4})\textsuperscript{2-}, [ZrO(OH)]\textsubscript{2}C\textsubscript{2}O\textsubscript{4}]\textsuperscript{2-}, [Zr(OH)]\textsubscript{2}(C\textsubscript{2}O\textsubscript{4})\textsubscript{3-} and [Zr(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}]\textsuperscript{4-} with oxalate ions in the pH range 3-7, the concentration of various fractions depending on their equilibrium conditions. During the course of our investigations, the pH of solutions A = 4.3 and B = 3.3 and after complete precipitation, the pH of the resultant solution was found to be in the range of 2.8-3.1. It was expected that ZrO(C\textsubscript{2}O\textsubscript{4})\textsuberscript{2-} (dissociation constant = 4.57 x 10\textsuperscript{-4})\textsuperscript{16} and TiO(C\textsubscript{2}O\textsubscript{4})\textsuberscript{2-} (dissociation constant = 5 x 10\textsuperscript{-4})\textsuperscript{18} species will be predominantly available during precipitation. During the addition of solution A to solution B, a finely dispersed precipitate was obtained. The chemical reactions occurring during the instantaneously mixing are given below.

\[
\begin{align*}
\text{ZrO(NO}_3)_2 + \text{Na}_2\text{C}_2\text{O}_4 &\rightarrow \text{ZrOC}_2\text{O}_4 + 2\text{NaNO}_3 \quad \text{(1)} \\
\text{ZrO(C}_2\text{O}_4) + \text{Na}_2\text{C}_2\text{O}_4 &\rightarrow \text{Na}_2\text{ZrO(C}_2\text{O}_4) \quad \text{(2)} \\
\text{Complex precursor} \\
\text{[Na}_2\text{ZrO(C}_2\text{O}_4)]_{0.525} + [\text{K}_2\text{TiO(C}_2\text{O}_4)]_{0.475} \\
+ \text{Pb(NO}_3)_2 &\rightarrow [(\text{Pb(Zr}_{0.525}\text{Ti}_{0.475})\text{O(C}_2\text{O}_4)]_{0.475} + 2[(\text{KN}_3)_{0.475} + [\text{NaNO}_3]_{0.525}] \quad \text{(3)}
\end{align*}
\]

The precipitate was carefully washed and then analysed. The analytical data is as follows:

\[
\begin{align*}
Pb = 38.85\% &\quad (\text{Zr} + \text{Ti})O = 16.6\% \quad \text{C}_2\text{O}_4 = 31.62\% \quad \text{and} \\
\text{H}_2\text{O} = 14.8\%. &\quad \text{The data revealed the final chemical composition of the precipitate to be} \\
Pb(Zr_{0.525}\text{Ti}_{0.475}) \cdot \text{O(C}_2\text{O}_4) \cdot 4\text{H}_2\text{O (PZTO).}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Table 1 — Comparative data on 'd' Å</th>
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<tbody>
<tr>
<td>PZO (Å)</td>
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<tr>
<td>--------</td>
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<tr>
<td>8.11 (s)</td>
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<tr>
<td>7.13 (m)</td>
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<td>5.71 (s)</td>
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<td>3.30 (w)</td>
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<tr>
<td>2.83 (s)</td>
</tr>
<tr>
<td>2.30 (w)</td>
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<td>2.02 (w)</td>
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<tr>
<td>1.97 (w)</td>
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<td>2.17 (w)</td>
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<tr>
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<td>2.26 (w)</td>
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<td>2.22 (w)</td>
</tr>
<tr>
<td>1.99 (m)</td>
</tr>
<tr>
<td>1.68 (w)</td>
</tr>
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s—strong, m—medium, w—weak.
PbZrO(C\(_2\)O\(_4\)\(_2\))(PZO)\(^{19}\) and PbTiO(C\(_2\)O\(_4\)\(_2\))(PTO)\(^{20}\)
It is seen that the observed 'd' values for our precipitated precursor do not match with those reported for PZO and PTO, indicating thereby the formation of different precursor by reaction (3) described above. Furthermore, the strong lines observed (d = 5.67, 3.93, 2.86) in PZTO are different than those reported for PZO/PTO beyond experimental accuracy. Furthermore, controlled pyrolysis of as-dried precipitate at various temperatures in air is utilized to study the evolution of mixture of cubic/tetragonal powders with lattice parameters (a = 4.04Å, c = 4.13Å) matching with the reported values\(^{21}\). It is examined by recording the XRD patterns of PZTO precipitate calcined at various temperatures and are shown in Fig. 1b. It is seen that the formation of cubic/tetragonal mixed phase material take place around the calcination temperature (T = 500°C) shown by DTA/TG/DTG without any traces of additional impurities. The broad and asymmetric X-ray diffraction peaks are well documented in Fig. 1b. The IR spectrum of as-dried precipitate in KBr pellet showed principal absorption band for \(\nu_c(C = O)\) at 1677 cm\(^{-1}\) and other bands due to \([\nu_c(C = O) + \nu(C - C)], [\nu_c(CO) + \delta(O - C - O)]\, \nu_c(CO) + \delta(O - C = O)] and [\delta(O - C = O) + \nu(MO)]\) vibrational modes are observed\(^{22}\) at 1412, 1289, 967 and 802 cm\(^{-1}\) respectively. The IR spectrum of
as-dried precipitate in KBr pellets calcined at 400°, 500° and 650°C for 6h in air in the range 4000-400 cm⁻¹ were recorded. The spectrum did not show oxalate, carbonate, water and carbon dioxide vibrational modes for samples calcined at 650°C for 6h. In metal-oxygen region²³ (300-700 cm⁻¹), bands at 590-650 cm⁻¹ were observed above calcination temperature 400°C/6 hrs. In Fig. 2, is presented the transmission electron micrograph of PZT powders obtained by calcination of PZTO at 650°C/6h in air. It indicated agglomerated submicron size (0.1-0.5 μm) of PZT particles with a variable shape.

The detailed study on electric, dielectric, piezoelectric and microstructural characterization of PZTO derived PZT powders is in progress.

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