pH dependent coprecipitated oxalate precursors - a thermal study of lead titanate

A. V. PRASADARAO, M. SURESH
Department of Inorganic and Analytical Chemistry, Andhra University, Visakhapatnam - 530 003, India

S. KOMARNENI
Materials Research Laboratory, The Pennsylvania State University, University park, PA 16802, USA
E-mail: komarneni@psu.edu

Formation of stoichiometric lead titanyl oxalate from mixed solutions of lead nitrate and potassium titanyl oxalate at different pH values was investigated by thermal analysis. At very low pH of ≈0.45 only lead oxalate was precipitated. Increase in pH from 0.45 to 2.5 did not yield stoichiometric lead titanyl oxalate. However, at pH 3, the precipitate obtained corresponded to lead titanyl hydroxy oxalate, which on heat treatment at 550°C for 1 h yielded phase pure PbTiO₃. Precipitation at pH 9 showed persistence of oxalate as an impurity. Mixed hydroxides of Pb and Ti with no traces of oxalate impurity occurred at pH 10.5. © *2001 Kluwer Academic Publishers*

1. Introduction

Lead titanate is a typical perovskite type ferroelectric which exhibits large pyroelectric coefficient and a high electromechanical coupling coefficient, the properties that are desirable for fabrication of pyroelectric detector and acoustic transducer devices respectively. Dense ceramics of pure PbTiO₃, however, cannot be fabricated because of microcraking resulting from cubic to tetragonal phase transformation at the curie temperature (490°C), as well as due to large anisotropic thermal expansion arising from constituent grains. The tendency of such microcracking can be controlled with suitable additives that inhibit grain growth [1–3]. Alternatively, synthesis of PbTiO₃ in the form of easily sinterable powder with very fine grains should minimise microcracking [4]. PbTiO₃ is normally prepared by solid-state reaction of PbO/PbCO₃ and TiO₂ at elevated temperatures. However, because of inherent limitations of this process, particularly in terms of resulting particle size and contamination during processing, several chemical methods have been advocated [5–11] among which oxalate coprecipitation route is apparently cost effective [12–15]. In all the precipitation methods TiCl₄ has been used as a precursor for titanium. The TiCl₄ precursor is extremely reactive even with atmospheric water vapour and requires temperatures as low as 0°C for proper dilution to avoid hydrolysis. This necessitates a quantitative estimation of Ti prior to the use of TiCl₄ aqueous solution in order to maintain the required stoichiometry of Pb to Ti. In some cases titanyl nitrate was used in place of TiCl₄ as a precursor for Ti [14, 15]. But the TiO(NO₃)₂ solution is inturn prepared from TiCl₄ via hydrolysis and subsequent dissolution in HNO₃. Van de velde [16] re-

ported that stoichiometric lead titanyl oxalate could not be synthesised above pH 1.5, while Bhattacharjee *et al.* [15] set the lower limit for synthesising the same at pH ≤ 0.45. The present investigation uses the readily available, water soluble potassium titanyl oxalate, as a precursor for Ti, and also discusses the effect of pH (from 0.45 to 10.5) on the formation of stoichiometric lead titanyl oxalate in terms of thermal decomposition of precipitates obtained at selected pH values.

2. Experimental

Flow diagram for the precipitation process in the present study is shown in Fig. 1. The used reagents, Pb(NO₃)₂ and K₂[TiO(C₂O₄)₂] 2H₂O (KTO) were of BDH AR quality. 100 ml of 0.1 M Pb(NO₃)₂ was added to 100 ml of 0.1 M KTO drop wise with constant stirring. The initial pH of the mixed solution was found to be around 0.2. Increase in pH of the mixed solution was achieved by the addition of ammonia. The precipitates obtained at pH values of 0.45 to 3.0 were washed with distilled water containing oxalic acid in order to maintain the required pH, while the precipitates obtained at pH 9.0 and 10.5 were washed with ammoniacal distilled water. Washings were carried out until the precipitates were free from nitrate and the samples were dried at room temperature. Thermal studies were carried out using a combined thermogravimetric analyser and differential thermal analyser (TG/DTA, 32, SEIKO, JAPAN). The final residues after heat treatment were identified using an X-ray diffractometer (Philips X'Pert system) with Cu Kα radiation. Oxalate content was analysed by permanganometry after digesting a known amount of sample in dilute H₂SO₄. Contents of Pb and Ti were

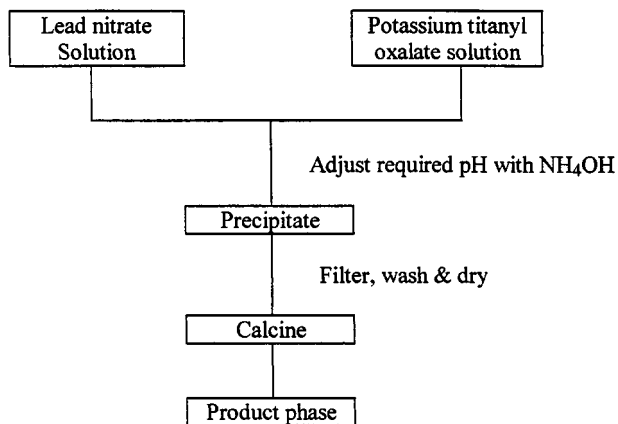*Figure 1* Flow diagram for the precipitation of precursor powder for PbTiO₃.

analysed gravimetrically by precipitating as $PbSO_4$ and Ti-cupferronate, respectively.

3. Results and discussion

Though stoichiometric barium titanyl oxalate can be easily prepared by mixing of $BaCl_2$ and KTO solutions [17] at pH values less than 3.0, synthesis of stoichiometric lead titanyl oxalate (PTO) does not seem to be so easy because of lower solubility of lead oxalate compared to lead titanyl oxalate complex in the pH range of 0.45 to 1.5. Further constraint on pH is due to rapid hydrolysis of Ti^{4+} above pH 3 leading to the formation of $TiO(OH)_2$ in preference to the complex. Hence, precipitates formed from mixed solution of $Pb(NO_3)_2$ and KTO at pH values of 0.45, 1.5, 2.0, 2.5, and 3.0 were studied by thermogravimetry (TG) and differential thermal analysis (DTA) to check whether the decomposition pattern of any of these precipitates matches with the previously reported TG of stoichiometric PTO [12, 13].

Fig. 2 depicts thermal behaviour of precipitate obtained at pH 0.45. The TG curve indicates only one weight loss of 24% in the temperature region from 275 to 400°C. The observed weight loss matches with the thermal decomposition for pure PbC_2O_4 (expected loss = 24%). The DTA curve also shows only one
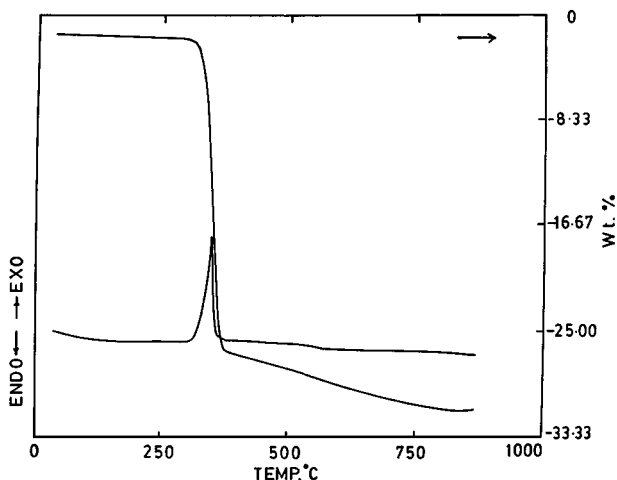
exothermic peak at 350°C. Chemical analysis of the precipitate showed $Pb : C_2O_4$ in the ratio of 1 : 1 with no titanium content, indicating the composition of the precipitate as PbC_2O_4. XRD pattern (shown in Fig. 6) of the above precipitate heat treated at 500°C for 1h indicated the presence of only PbO. Thermal behaviour of precipitates obtained at pH 1.5, 2.0, and 2.5 are shown in Fig. 3. The respective weight losses for the above precipitates were found to be 30%, 29.6% and 35.4%. In all these cases, the observed weight loss was higher than that expected for pure lead oxalate and less than that expected for stoichiometric PTO. XRD patterns of the above precipitates heat treated at 500°C for 1h are presented in Fig. 6. From the XRD patterns it is evident that the residues were two phase mixtures of PbO
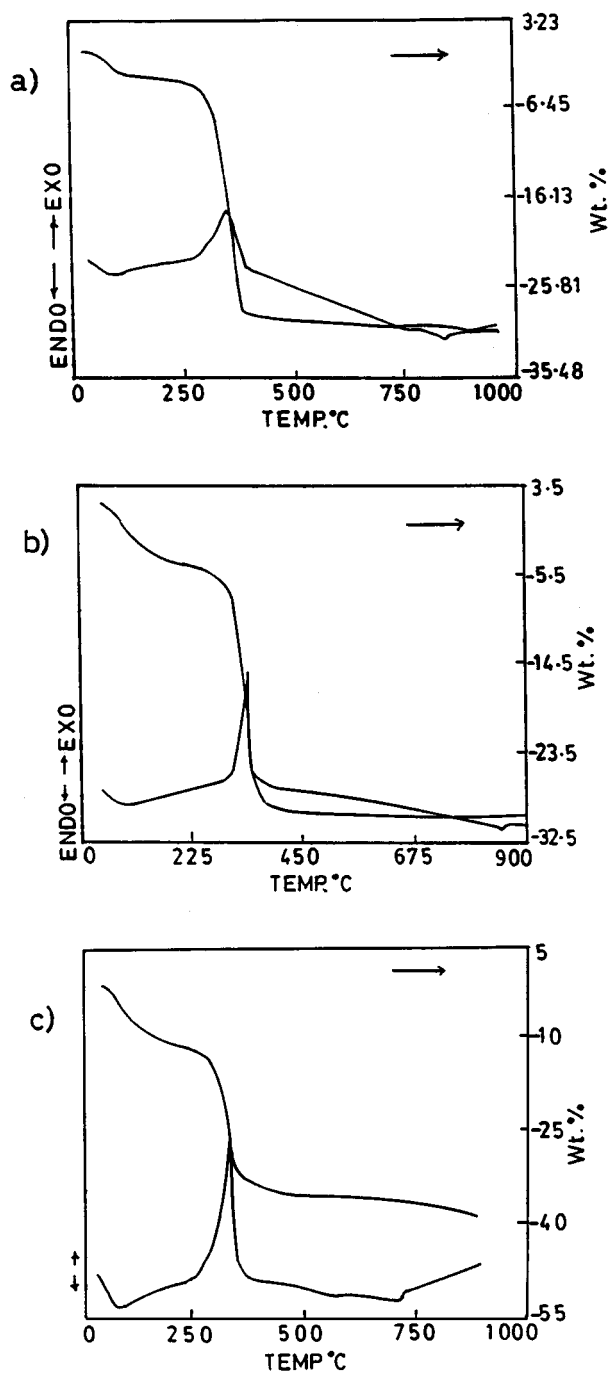

Figure 2 TG and DTA curves of precipitate at pH 0.45.

Figure 3 TG and DTA curves of precipitate at pH values of a) 1.5, b) 2.0 and c) 2.5.
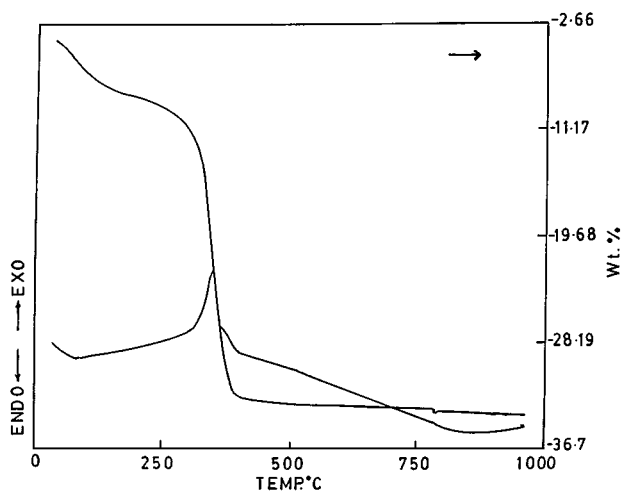
Figure 4 TG and DTA curves of precipitate at pH 3.0.

and $PbTiO_3$ suggesting that the initial precipitates were mixtures of lead oxalate and lead titanyl oxalate of varying proportions depending on pH. These results agree with the report of Van de velde [16] that beyond pH 0.45 PbC_2O_4 is precipitated together with PTO. TG and DTA curves for precipitate obtained at pH 3 are shown in Fig. 4. The observed weight loss was 34.3% which is close to the thermal decomposition of lead titanyl hydroxy oxalate, $Pb[TiO(OH)_2C_2O_4]4H_2O$. (Theor. loss = 34.8%). Quantitative analysis of the precipitate indicated $Pb : Ti : C_2O_4$ content in the ratio $1 : 1 : 1$ which excludes the supposition of a stoichiometric dioxlate derivative of composition $Pb[TiO(C_2O_4)_2]$ $4H_2O$. Further, the precipitate heat treated at 550°C for 1h yielded a phase pure $PbTiO_3$, the XRD pattern of which is given in Fig. 6.

Since it can be noticed from the solubility diagrams for lead hydroxide and titanium hydrous oxide systems [18], that lead and titanium can be coprecipitated at pH 9.0–10.0, precipitation in the present study has also been done at pH 9. Thermal behaviour of precipitate obtained at pH 9, shown in Fig. 5 indicates a total weight loss of 16.7%. The corresponding DTA curve showed one endothermic peak at 87°C and two exothermic peaks - one at 320 and the other at 512°C. The endothermic peak at 87°C may be assigned to dehydration of titanium hydrous oxide while the first exothermic peak may be assigned to two factors - namely, crystallisation of anatase and thermal decomposition of lead oxalate impurity present along with lead hydroxide precipitate. The exothermic peak at 512°C was due to phase transition of anatase to rutile. The precipitate heat treated at 600°C for 1 h yielded phase pure $PbTiO_3$, (Fig. 6). The presence of oxalate impurity could be completely eliminated by increasing precipitation pH to 10.5. Thermal behaviour of the precipitate obtained at pH 10.5 is shown in Fig. 5 which shows no exothermic peak in the temperature range of 320–350°C. The observed weight loss of 19.1% is in close agreement with the expected weight loss (Theoretical weight loss = 19.2%) for mixed hydroxides $Pb(OH)_2$ $H_2O + TiO(OH)_2$ H_2O. Hence, the optimum pH for coprecipitation of Pb and Ti in the present system is 10.5 and not 9.0. Chemical analysis of the precipitates
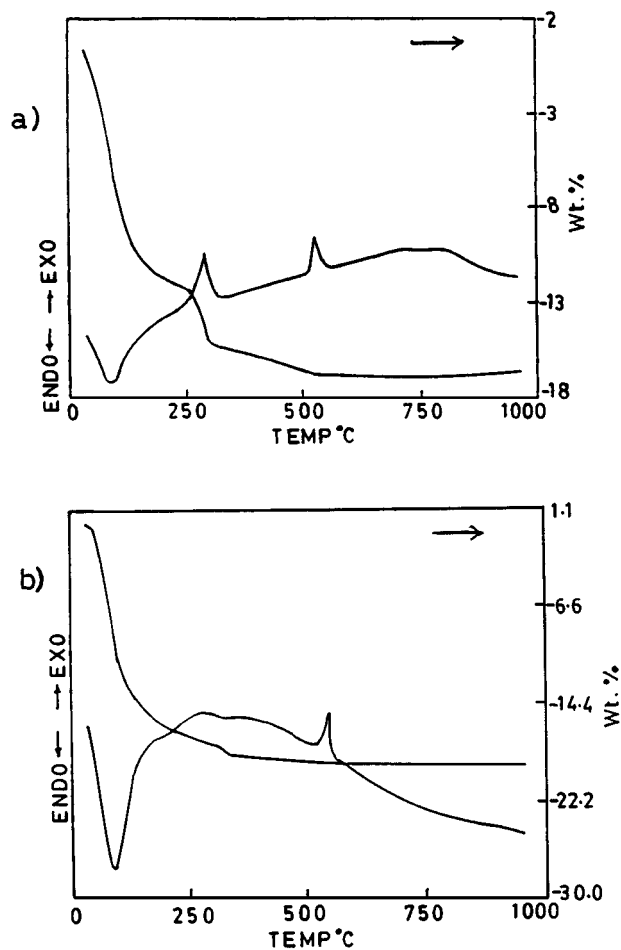

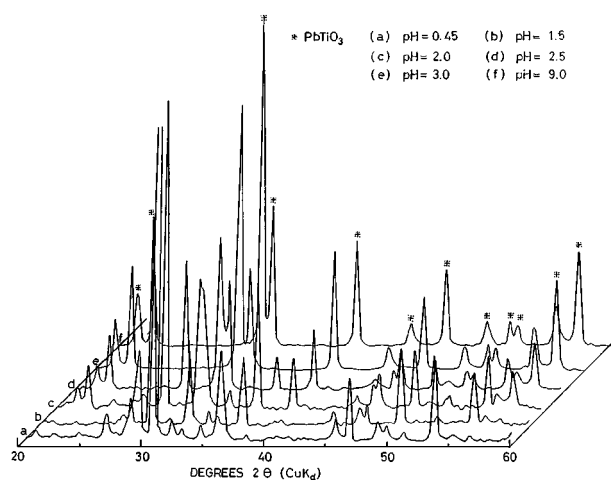*Figure 5* TG and DTA curves of precipitates at pH values of a) 9.0 and b) 10.5.

Figure 6 XRD patterns of the precipitates obtained at different pH values and heat treated at a) 500°C, b) 500°C, c) 500°C, d) 500°C, e) 550°C, f) 600°C for 1 h.

obtained at pH = 9.0 and 10.5 also support the above compositional assignments.

4. Conclusions
From the above results it may be concluded that no stoichiometric lead titanyl oxalate of the form Pb $[TiO(C_2O_4)_2]4H_2O$ resulted at any pH from 0.45 to 2.5. However, at pH 3 stoichiometric lead titanyl hydroxy

oxalate Pb [TiO(OH)$_2$ C$_2$O$_4$] 4H$_2$O was formed, which on thermal decomposition at 550°C for 1h yielded phase pure PbTiO$_3$. Also at pH 10.5 both lead and titanium were precipitated as hydroxides.

References

1. G. KING and E. K. GOO, *J. Amer. Ceram. Soc.* **73** (1990) 1534.
2. T. SUWANNASIRI and A. SAFARI, *ibid.* **76** (1995) 3155.
3. A. V. PRASADA RAO, A. I. ROBIN and S. KOMARNENI, *Ferroelectric. Lett.* **21** (1996) 141.
4. M. AWANO, K. NAKAMURA, T. YAMADA and H. TAKAGI, *Powder. Matellurgy Intl.* **21** (1989) 23.
5. L. DEL OLMO, M. L. CALZADA and B. JIMENEZ, *Ferroelectrics* **94** (1989) 167.
6. J. A. DARIES and S. DUTREMEZ, *J. Amer. Ceram. Soc.* **72** (1990) 2570.
7. G. R. FOX, E. BREVAL and R. E. NEWNHAM, *J. Mat. Sci.* **26** (1991) 2566.
8. M. LEE and B. CHOI, *J. Amer. Ceram. Soc.* **74** (1991) 2309.
9. M. L. CALZADA and J. DE FRUTOS, *J. Mater. Sci. Mater. in Electr* **4** (1993) 83.
10. L. B. ARCHER, C. D. CHANDLER, R. KINGSBOROUGH and M. J. HAMPDEN-SMITH, *J. Mater. Chem.* **5** (1995) 151.
11. D. PAIK, A. V. PRASADA RAO and S. KOMARNENI, *Mater. Lett.* **32** (1997) 97.
12. B. V. STRIZKOV. A. V. LAPITSKII, L. G. VLASOV and A. I. TSVETKOV, *Zh. Prikl. Khim.* **34** (1961) 673.
13. G. M. H. VAN DE VELDE and P. J. D. ORANJE, *Thermo Chim. Acta.* **14** (1976) 269.
14. H. S. GOPALAKRISHNA MURTHY, M. SUBBARAO and T. R. N. KUTTY, *J. Inorg. Nucl. Chem.* **38** (1976) 417.
15. S. BHATTACHARJEE, M. K. PARIA and H. S. MAITI, *Mater. Lett.* **13** (1992) 130.
16. G. M. H. VAN DE VELDE and J. VENSELLAR, *J. Inorg. Nucl. Chem.* **39** (1977) 1363.
17. A. V. PRASADARAO, M. SURESH and S. KOMARNENI, *Mater. Lett.* **39** (1999) 359.
18. J. CHOY, Y. HAN and J. KIM, *J. Mater. Chem.* **5** (1995) 65.