Mixed Hydroxide Precursors for $La_2Ti_2O_7$ and $Nd_2Ti_2O_7$ by Homogeneous Precipitation

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Abstract. Feasibility of formation of stoichiometric precursors of either $M_2 (TiO)_2(C_2O_4)_5$ $4H_2O$ (M $=$ La and Nd) or coprecipitated hydroxides of $M(OH)_3 + TiO(OH)_2$ was investigated by two solution routes at different pH values. Composition of precipitates obtained at pH $= 7.0$ by coprecipitation method starting from La or Nd nitrates and potassium titanyl oxalate corresponded to a physical mixture of La or $Nd(C_2O_4)_3$ $9.5H_2O$ and $TiO(OH)_2 \cdot H_2O$ which on thermal decomposition did not yield phase pure $M_2Ti_2O_7$. However, precipitation from La or Nd nitrates and titanium tertrachloride by urea hydrolysis yielded homogeneous mixture of hydroxides of La or Nd and Ti, which on pyrolysis at 950°C yielded phase pure $La_2Ti_2O_7$ and $Nd_2Ti_2O_7$. Use of potassium titanyl oxalate as precursor for Ti, led to selective precipitation of La or Nd oxalate even at pH as low as 0.1 leading to sequential precipitation of La or Nd oxalate followed by Ti hydroxide at pH $= 3.0$. The resultant precipitate on pyrolysis underwent typical solid-state reaction.

Keywords: coprecipitation, urea hydrolysis, lanthanum titanate, neodymium titanate

1. Introduction

Lanthanum dititanate, $La_2Ti_2O_7$ and Neodymium dititanate, $Nd_2Ti_2O_7$ belonging to the family of perovskite layer structures crystallize in monoclinic symmetry with a space group $P2_1$. Both the above are effective ferroelectric substances with high curie temperatures and coercive fields [1–3]. Their thermal Stability at elevated temperatures along with their low dielectric loss at microwave frequencies make them suitable materials for high frequency applications [4, 5]. These titanates also exhibit piezoelectric properties, which make them useful for high temperature transducer applications. The synthesis of $La_2Ti_2O_7$ and $Nd_2Ti_2O_7$ in polycrystalline form has been reported using colloidal precipitation, liquid mix technique, evaporative decomposition of solutions, molten salt synthesis, sol-gel and polymeric complex formation methods [6–11]. Nevertheless, ceramics of $La_2Ti_2O_7$ and $Nd_2Ti_2O_7$ are being fabricated thus for only by solid-state reactions of the constituent oxides at temperatures around 1200°C.

Since cost-effective powders of uniform particles exhibiting good sinterability and fine grained size are desirable for high quality device fabrication, low temperature chemical synthesis via precipitation from homogeneous solution (PFHS) is explored in the present investigation.

2. Experimental

The reagents used were La_2O_3, Nd_2O_3, $TiCl_4$ and $K_2[TiO(C_2O_4)_2]2H_2O$ (KTO). $La(NO_3)_3$ and $Nd(NO_3)_3$ were prepared by dissolving calculated amounts of La_2O_3 and Nd_2O_3, respectively in minimum amount of HNO_3 (Basynth Analar). In the coprecipitation method mixed solutions were prepared by adding equal volumes of equimolar $La(NO_3)_3$ or $Nd(NO_3)_3$ and KTO with constant stirring. Initial pH of mixed solution was found to be around 0.1. Dilute ammonia was added to obtain the desired pH. The precipitates obtained at pH equal to 2.5 and 7.0 were washed with water adjusted to their respective pH values. After
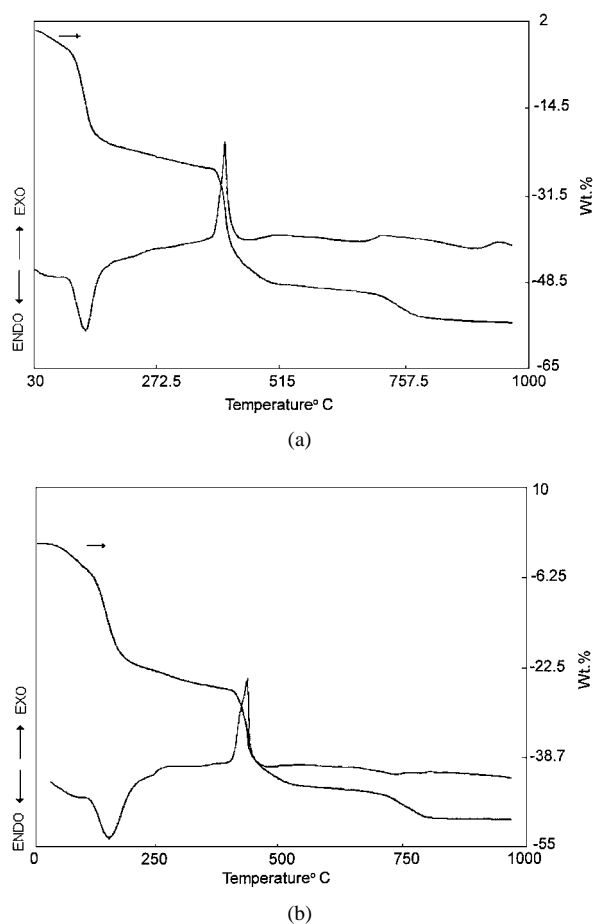
Fig. 1. TG and DTA curves of coprecipitate obtained from La nitrate and KTO at (a) pH = 2.5 and (b) pH = 7.0.

ensuring that the precipitates were free from nitrate, samples were air dried at room temperature.

In homogeneous precipitation, individual mixtures of $La(NO_3)_3$ with $TiCl_4$ and $Nd(NO_3)_3$ with $TiCl_4$ were prepared from 50.0 ml each of 0.1 molar aqueous solutions. Intial pH of mixed solution was found to be around 0.05. To the mixed solution, a few drops of methyl red indicator and 25 gms of urea were added. The solution was boiled gently until the indicator colour changed from red to pale yellow and the precipitate obtained was allowed to cool down to room temperature and washed free from nitrate and chloride. The samples were then air dried at room temperature. Thermal studies of the resultant precipitates were carried out using a combined thermogravimetric analyser and differential thermal analyser, model TG/DTA-32

(Seiko). Final residues after specified heat treatments were characterized by powder X-ray diffraction using an X-ray diffractometer, X' Pert system (Philips) with Cu K_α radiation. Oxalate content was analysed by permangonometry and Ti content was determined gravimetrically as Ti-Cupferronate.

3. Results and Discussion

In view of literature reports of the formation of $M[TiO(C_2O_4)_2] \cdot xH_2O$ where M = Ba, Sr, Ca and Pb by coprecipitation [12–15] and $Ba[TiO(C_2O_4)_2]$ $4H_2O$ by PFHS [16], feasibility of the formation of coprecipitated precursors for La and Nd analogous to La_2 $(ZrO)_2(C_2O_4)_5 \cdot 4H_2O$ [17] from mixed solutions of lanthanum nitrate and KTO was studied at pH = 2.5.
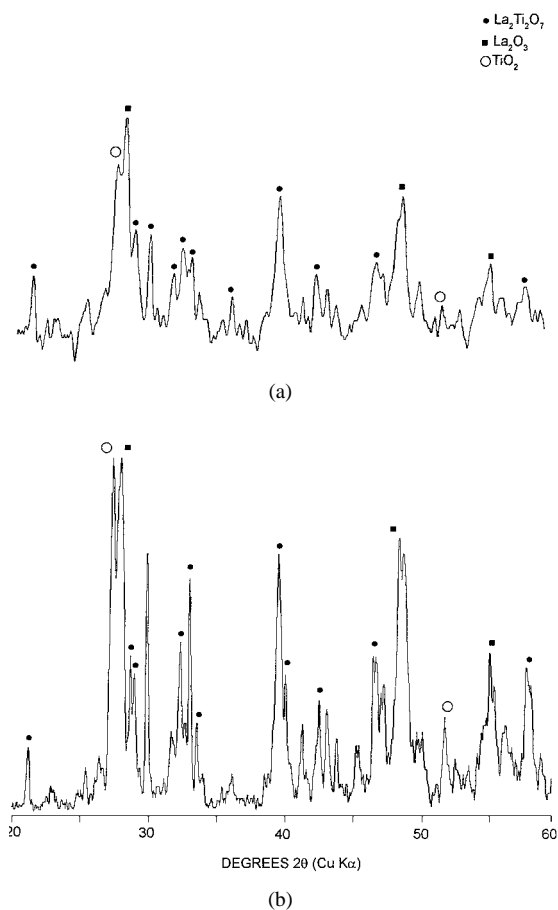

Fig. 2. XRD patterns of precipitate obtained from coprecipitation of La nitrate and KTO at pH = 7.0 and heat treated at (a) 850°C and (b) 1000°C for 1 h.

Thermal behavior of resultant precipitate shown in Fig. 1(a), indicates three weight losses in temperature regions of 50–300, 320–540 and 670–850°C. Total weight loss obtained upto 850°C was 55.6%. From the observed thermal decomposition pattern, the intermediates at 300, 600 and 850°C may be assigned to $La_2 (C_2O_4)_3$, $La_2O_2CO_3$ and La_2O_3, respectively. Dehydration and thermal decomposition reactions involved along with their theoretical and practical weight losses are given in Table 1. Since chemical analysis of the precipitate did not show the presence of any Ti, the obtained precipitate must only be $La_2(C_2O_4)_3$ $9.5H_2O$. Corresponding differential thermal analysis (DTA) curve showed one sharp endothermic peak at 135°C followed by another sharp exothermic peak at 405°C. These peaks fall respectively within the temperatures of dehydration and decomposition steps discussed above. XRD pattern of the precipitate heat treated at 850°C for 1h indicated the residue to be La_2O_3. Thermal behavior of precipitate obtained at pH = 7.0 is shown in Fig. 1(b). Based on the observed weight loss, intermediates corresponding to plateaus in this thermogram may be assigned to $La_2(C_2O_4)_3$, $2TiO_2$, $La_2Ti_2O_5CO_3$ and $La_2O_3 + 2TiO_2$. Corresponding dehydration and decomposition steps along with their theoretical and

practical weight losses are also presented in Table 1. Since DTA curve of the precipitate did not show any exothermic peak above 500°C corresponding either to phase transformation of anatase to rutile or to crystallisation of $La_2Ti_2O_7$, the precipitate was subjected to different heat treatment studies. XRD patterns of the precipitate heat treated at temperatures of 850 and 1000°C are presented in Fig. 2. These patterns showed peaks characteristic of La_2O_3, TiO_2 and $La_2Ti_2O_7$. It may therefore be surmised that $La_2(C_2O_4)_3$ $9.5H_2O$ and $TiO(OH)_2$ H_2O precipitated separately rather than simultaneously. Hence the reaction between lanthanum oxalate and titanium oxy hydroxide required temperatures higher than 1000°C to yield phase pure $La_2Ti_2O_7$.

In order to overcome such preferential precipitation of lanthanum oxalate, $TiCl_4$ was used in place of KTO and precipitation was carried out by means of urea hydrolysis, so as to obtain both La and Ti hydroxides from homogeneous precipitation. A thermogram of the precipitate obtained by urea hydrolysis depicted in Fig. 3 shows a continuous weight loss from room temperature to 850°C with a weight loss equal to ~33.0%. The observed weight loss agrees well with theoretical weight loss for $La(OH)_3 3H_2O + TiO(OH)_2 H_2O$. Related

Table 1. Summary of results obtained by thermal analysis of precipitates.

| Proposed thermal decomposition steps	% Weight loss	
	Theor.	Practl.
1. Coprecipitation route:		
At pH = 2.5		
$La_2 (C_2O_4)_3$ $9.5 H_2O \rightarrow La_2 (C_2O_4)_3 + 9.5 H_2O$	24.0	25.7
$\rightarrow La_2O_2CO_3 + 2CO_2 + 3 CO + 9.5 H_2O$	48.1	48.9
$\rightarrow La_2O_3 + 3CO_2 + 3 CO + 9.5 H_2O$	54.3	55.7
$Nd_2 (C_2O_4)_3$ $9.5 H_2O \rightarrow Nd_2 (C_2O_4)_3 + 9.5 H_2O$	23.7	–
$\rightarrow Nd_2 (CO_3)_3 + 3CO + 9.5 H_2O$	35.3	–
$\rightarrow Nd_2O_3 + 3CO_2 + 3CO + 9.5 H_2O$	53.5	52.6
At pH = 7.0		
$La_2 (C_2O_4)_3$ $9.5 H_2O + 2 TiO(OH)_2$ H_2O		
$\rightarrow La_2(C_2O_4)_3 + 2 TiO_2 + 13.5 H_2O$	25.7	26.5
$\rightarrow La_2Ti_2O_5CO_3 + 2CO_2 + 3 CO + 13.5 H_2O$	48.1	48.9
$\rightarrow La_2O_3 + TiO_2 + 3CO_2 + 3 CO + 13.5 H_2O$	49.0	49.8
$Nd_2 (C_2O_4)_3$ $9.5 H_2O + 2TiO(OH)_2H_2O$		
$\rightarrow Nd_2 (C_2O_4)_3 + 2 TiO_2 + 13.5 H_2O$	25.4	–
$\rightarrow Nd_2O_3 + TiO_2 + 3CO_2 + 3CO + 13.5 H_2O$	48.1	45.6
2. Urea hydrolysis at pH = 7.0		
$2La(OH)_3 3H_2O + 2TiO(OH)_2H_2O \rightarrow La_2Ti_2O_7 + 13 H_2O$	32.0	32.0
$2Nd(OH)_3 3H_2O + 2TiO(OH)_2H_2O \rightarrow Nd_2Ti_2O_7 + 13 H_2O$	32.0	32.0
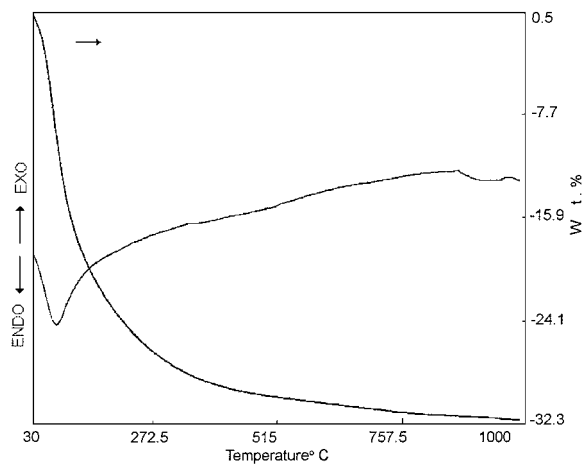
Fig. 3. TG and DTA curves of precipitate obtained from La nitrate and TiCl₄ by PFHS.
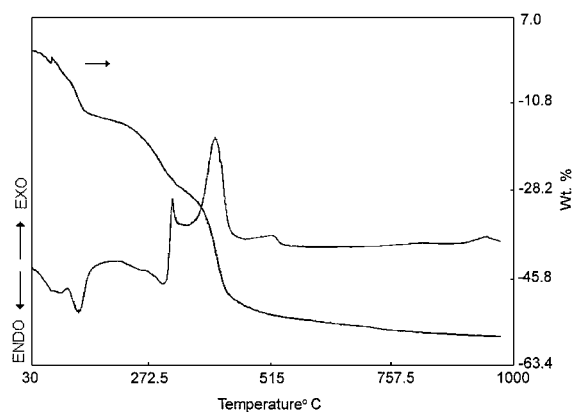
(a)
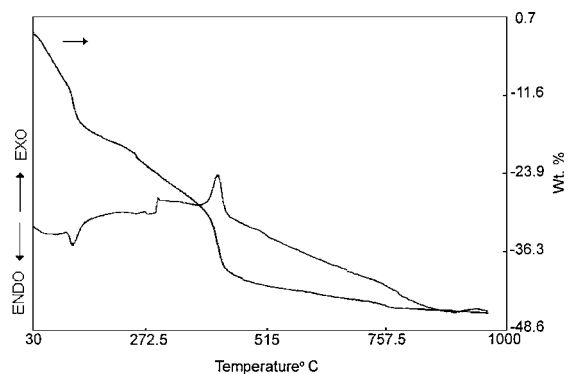
(b)

Fig. 4. TG and DTA curves of coprecipitates obtained from Nd nitrate and KTO at (a) pH = 2.5 and (b) pH = 7.0.

theoretical and experimental weight loss steps are given in Table 1. Powder XRD pattern of the above precipitate heat treated at 950°C for 1h indicated the presence of phase pure $La_2Ti_2O_7$. XRD patterns of the same precipitate heat treated at 850°C showed the powders to be amorphous.

Thermal behavior of precipitates of Nd-Ti system obtained by coprecipitation from KTO and $Nd(NO_3)_3$ as starting materials at pH values 2.5 and 7.0 are shown in Fig. 4. Unlike La-Ti system, thermal decomposition of precipitates in this system indicated no intermediate compound formation. Probable decomposition mechanisms for this system are given in Table 1.
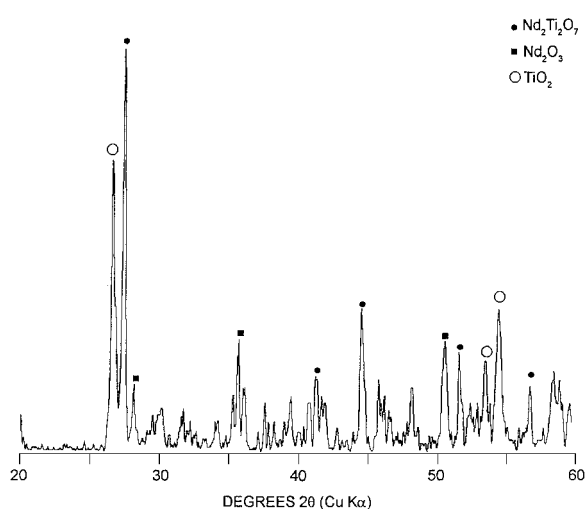

Fig. 5. XRD pattern of precipitate obtained from coprecipitaion of Nd nitrate and KTO at pH = 7.0 and heat treated at 1000°C for 1 h.
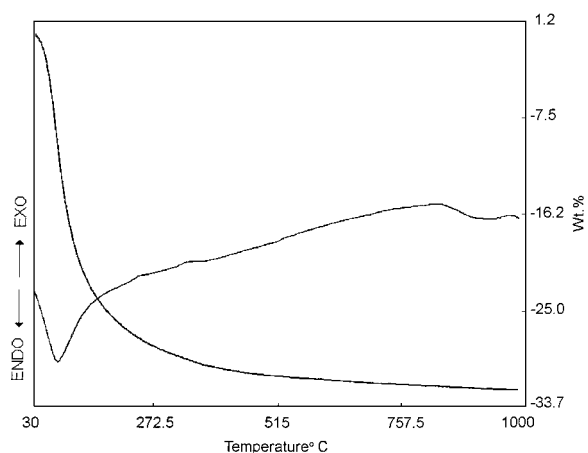

Fig. 6. TG and DTA curves of precipitate obtained from Nd nitrate and TiCl₄ by PFHS.

Corresponding XRD pattern of precipitate heat treated at 1000°C for 1 h depicted in Fig. 5 did not show phase pure $Nd_2Ti_2O_7$. However, TG of precipitate obtained by urea hydrolysis presented in Fig. 6 showed a continuous weight loss from room temperature to 850°C. Observed weight loss of the precipitate corresponded to decomposition of $Nd(OH)_3$ and $TiO(OH)_2 H_2O$. Proposed stages of thermal decomposition mechanism for the above is also given in Table 1. Powder XRD pattern of the precipitate heat treated at 950°C for 1 h showed the presence of phase pure $Nd_2Ti_2O_7$ only.

4. Conclusions

From the above results, it may be concluded that starting from aqueous solutions of KTO and $La(NO_3)_3$, stoichiometric precursor of the form $La_2[(TiO)_2(C_2O_4)_5]$ $4H_2O$ could not be prepared in the pH range of 0.5 to 7.0 since lanthanum oxalate preferentially precipitated prior to pH = 3.0. Further increase in pH precipitated Ti as $TiO(OH)_2$. Thermolysis of mixed precipitate of lanthanum oxalate and titanium hydroxide yielded $La_2Ti_2O_7$, La_2O_3 and TiO_2 just as a typical solid-state reaction between the La_2O_3 and TiO_2. However, simultaneous precipitation of hydroxides of La and Ti could be achieved by precipitation from homogeneous solution with urea hydrolysis using $TiCl_4$ and La or Nd $(NO_3)_3$ as starting materials. Heat treatment of the precipitate at 950°C indicated formation of phase pure $La_2Ti_2O_7$ or $Nd_2Ti_2O_7$ only. The precipitates obtained by urea hydrolysis may serve as cost-effective precursors for La and Nd dititanates.

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