# ATTAINMENT OF  LEAD TITANATE
# Through the thermal decomposition of coprecipitated 8-hydroxyquinolinate precursors

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## Abstract

Crystalline $PbTiO_3$ was obtained through the thermal decomposition of 8-hydroxyquinolinate of lead(II) and that of titanium(IV), which was monitored by TG/DTG/DTA under different atmospheric conditions and with varying heating rates. The compound was prepared from adding 8-hydroxyquinoline solution in the solution of metallic ions Pb(II):Ti(IV) (1:1) under constant stirring at 3°C, having the pH adjusted to 10. The results of these investigations show that different thermal behavior related to the precursor occurred and also the consequent formation of residues which have different crystallinities. No carbonate residues from the thermal decomposition could be determined by XRD and IR. Only $PbTiO_3$ was observed and confirmed by DSC at 470°C, temperature lower than the tetragonal-cubic transition.

**Keywords:** 8-hydroxyquinoline, $PbTiO_3$, precursor powder

## Introduction

Several solution based preparative methods for precursor powders to obtain mixed oxides, like sol-gel and coprecipitation, have been described in [1–8] as alternatives to the solid-state reaction routes.

The coprecipitation of chelates, one of those methods reported in literature has been mentioned, once several chelating agents [9–14] and their derivative compounds present high stability in the precipitation medium as well as in room atmosphere, besides having a defined stoichiometry. In addition, it can be carried out in a higher homogeneity and purity medium, which affect the thermal decomposition steps and thus originating a final product with improved features, different crystallinity and particle sizes [15].

In this work, we present results when obtaining a mixed oxide $PbTiO_3$ via thermal decomposition of precursor powders, prepared by coprecipitation, using 8-hydroxyquinoline as the chelating agent, in different atmospheres and heating rates.

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## Materials and methods

A solution containing the metallic cations in a molar ratio of 1:1 (Pb(II):Ti(IV)) was prepared, from lead nitrate (Synth) and metallic titanium (Carlo Erba) and kept at pH close to zero to avoid the formation of the metal hydroxides. 8-hydroxyquinoline was used as a complex forming agent, in 10% excess, and dissolved in an ethanol/water mixture (4:1, *v*:*v*) followed by the adjustment of pH adjusted to 10 with addition of aqueous ammonium hydroxide. Under constant stirring and temperature, at 3°C, the 8-hydroxyquinoline solution was added to the one containing the metallic cations at a rate of 0.232 mL min$^{-1}$, keeping the pH at 10 by simultaneous addition of an aqueous solution of ammonium hydroxide. The precipitate was filtered, dried for 24 h in an oven at 60°C and stored in a desiccator over anhydrous calcium chloride.

The precipitate was characterized by elemental analysis (N, C, H) in a CE Instruments Elemental Analyzer, model EA 1110-CHNS-O. The thermal decomposition was followed by recording the simultaneous curves in a TG/DTA equipment, model SDT 2960, from TA Instruments, under dynamic atmosphere of synthetic air or nitrogen, using heating rates of 1, 10 and 20°C min$^{-1}$. The $\Delta H$ of decomposition was calculated by the equation:

$$\Delta Hm = kA \tag{1}$$

where $\Delta H$ is the reaction energy, $m$ is the mass loss in the reaction of the decomposition, $k$ is calibration constant and $A$ is the area of the peak observed in the DTA curve, having metallic aluminium as reference material [16].

The residues were characterized through XRD, using a HGZ4/β horizontal diffractometer in a Bragg–Bretano assemblance and CoK$_\alpha$ radiation; as well as IR by using a Nicolet infrared spectrometer, model FT Impact 400, being the samples prepared as KBr pellets; in addition, the DSC curves were recorded in the equipment from TA Instruments, model DSC 2910, using dynamic nitrogen atmosphere and a heating rate of 10°C min$^{-1}$.

## Results and discussion

As both of 8-hydroxyquinolinates of lead and of titanium occur below pH 8, the pH was kept at 10 so that the total amount of metal could be precipitated almost simultaneously. The hydrolysis of the metallic ions was not observed even in the alkaline region because of the high formation constant (Kf) of 8-hydroxyquinolinates [17, 18] originating from the chelate rather than the hydrate oxides. This could be confirmed through elemental analysis, where it could be verified that the resulting compound is a mixture of the lead and of titanium chelates [19–21], presenting the following stoichiometry: Pb(C$_9$H$_6$NO)$_2$·TiO(C$_9$H$_6$NO)$_2$·1.5H$_2$O, and could be confirmed through TG curves under dynamic synthetic air atmosphere, Fig. 1, considering PbTiO$_3$ as the final residue.

TG curve obtained under synthetic air atmosphere and at a heating rate of 10°C min$^{-1}$, Fig. 1a, shows four steps of mass loss, better defined by the peaks observed in DTG curve. The first one is attributed to the dehydration of the compound
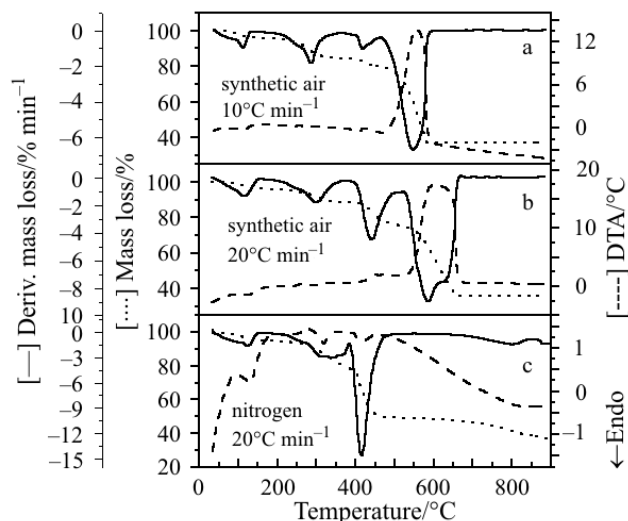
**Fig. 1** ··· – TG, —— – DTG and ---- – DTA curves of the precursor powder, obtained under different atmospheric and heating rate conditions

indicated by an endothermic peak in the DTA curve. The three other steps were ascribed to the decomposition/oxidation of the anhydrous chelate, which can be seen by the exothermic peaks in the DTA curve.

Four steps of mass loss were observed in the TG curve, which was obtained under dynamic synthetic air atmosphere and at a heating rate of $20°C$ $min^{-1}$, Fig. 1b. They can be ascribed to the same behavior indicated before, e.g., the dehydration followed by the decomposition/oxidation of the chelate. However, the higher the temperature at which the thermal decomposition occurs, the higher the heating rate and changes are in the amount of mass loss in each step, except for the dehydration one, indicating some alterations of the thermal decomposition mechanism. $\Delta H$, from the decomposition of the last step of mass loss, was verified by an intense exothermic peak, being 9.3 and 18.8 kJ $g^{-1}$, at heating rates 10 and $20°C$ $min^{-1}$, respectively.

TG/DTG/DTA curves obtained under dynamic nitrogen atmosphere and at a heating rate of $20°C$ $min^{-1}$ are shown in Fig. 1c. The first step of mass loss, attributed to the dehydration of the compound, occurs in the same way as it occurred in synthetic air atmosphere, but differently to the following steps, in which the alterations are due to the absence of oxygen in the atmosphere resulting in carbonate residues.

DTA curve presents endothermic peaks with relation to the thermal decomposition of the anhydrous compound, which is incomplete up to the final temperature of the analysis, as verified in the TG curve.

X-ray diffractograms indicate just the presence of $PbTiO_3$ oxide, with higher crystallinity degree for the residue at $20°C$ $min^{-1}$, which was due to the faster release of energy, thus causing greater influence in the final mixed oxide formation.

The bands of absorption of the infrared spectra are assigned, as expected, only to the metal-oxygen bonds and no bands of carbonate material were detected, as already verified through X-ray diffractograms.

The evolution of the precursor powder phase, at different temperatures, under synthetic air and at a heating rate of 20°C min$^{-1}$, was followed by XRD, Fig. 2, where the presence of the crystalline phases of PbTiO$_3$ at higher temperatures could be seen. From 500 to 600°C, the PbO phase also occurred, and finally, only at 800°C, PbTiO$_3$ tetragonal was confirmed.

The precursor powder was analyzed through TG/DTA under synthetic air and 1°C min$^{-1}$, Fig. 3, where it was shown that the thermal decomposition ends up to 470°C, temperature lower than the tetragonal-cubic phase transition.
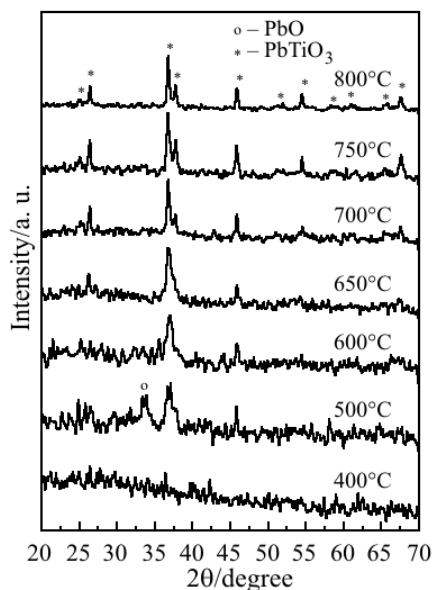


**Fig. 2** XRD of the evolution of precursor powder phase as a function of the tempera-
ture, in flowing synthetic air and heating rate of 20°C min$^{-1}$



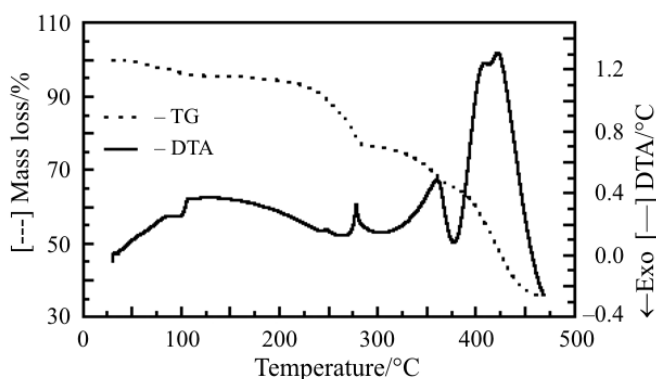**Fig. 3** ··· – TG and —— – DTA curves of the precursor powder, obtained under dynamic
synthetic air atmosphere and heating rate of 1°C min$^{-1}$

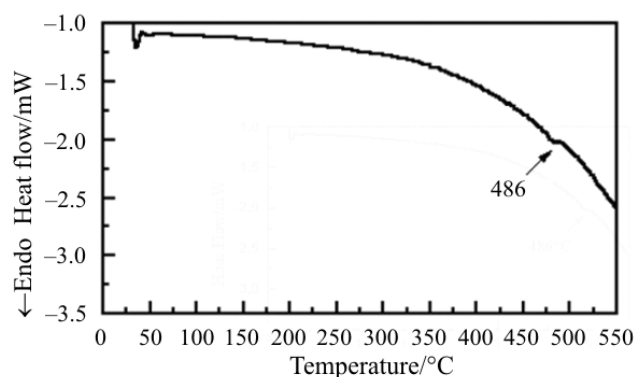**Fig. 4** DSC curve of the residue, obtained under dynamic synthetic air atmosphere and heating rate of 10°C min$^{-1}$

The residue obtained at 470°C was analyzed through DSC, Fig. 4, and the analysis showed the existence of the tetragonal-cubic phase transition up to 486°C, which confirmed the obtainment of the PbTiO$_3$ oxide.

## Conclusions

This work presents experimental data on the use of 8-hydroxyquinoline to obtain the mixed oxide, PbTiO$_3$, via thermal decomposition. It was found that the same residue was obtained at different heating rates, but showing different crystallinity. It was also observed that the mixed oxide PbTiO$_3$ can be obtained at temperatures below the tetragonal-cubic phase transition, thus preventing material fractures.

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