

## TITANATES FROM OXIME-CONTAINING COMPLEX PRECURSORS

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The paper proposes a new way of  $\text{MTiO}_3$  preparation – thermal decomposition of  $[\text{M}(\text{L}-\text{H})_2\text{Ti}(\text{OH})_2](\text{OH})_2$  heterodinuclear complexes (L = 1-phenyl -2(1'-piperidinyl) ethanone oxime; M=Co,Ni,Cu). The complex precursors have been characterized by electronic and IR spectra, molar conductivity, magnetic properties and TG-DTA analysis. The processing parameters (temperature and time of calcination) for  $\text{MTiO}_3$  preparation as well as IR spectra, XRD analysis and electrical properties of the obtained titanates have also been studied and discussed.

### INTRODUCTION

The pure or doped titanates of some 3d transition metals (manganese, iron, cobalt, nickel, copper) form a class of mixed oxides with many technical applications due to their electrical (dielectric, ferroelectric, piezoelectric), mechanical and/or catalytic properties.<sup>1-4</sup>

The microporous solids (prepared by pillaring layer structured manganese titanate,  $\text{Rb}_x\text{Mn}_x\text{Ti}_{2-x}\text{O}_4$  with silica) chemical modified by loading various kinds of metals by cation exchange and impregnation method showed a high catalytic activity for the oxidation of carbon monoxide with oxygen (the higher activity was obtained for the sample with copper content when the CO conversion of more than 90% was achieved at only 60°C).<sup>5</sup>

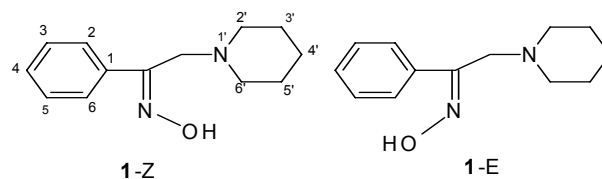
The literature also studied bismuth lead nickel titanates as a new group of piezoelectric ceramics with mechanical strength higher than that of the conventional PZT system.<sup>6</sup>

A material with cubic structure,  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  was also studied for its large dielectric response, the temperature dependence of which has not been seen in any existing material.<sup>7</sup> And the examples can continue.

Like in the case of other mixed oxides, the morphology and physical properties of titanates depend on their preparation method and thermal treatment, which affects the dispersion of

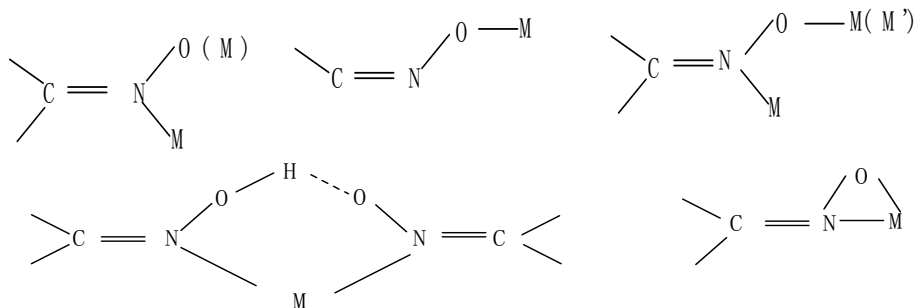
components. Therefore, considerable research work has been made to develop mixed oxides synthesis methods in general and titanates in particular. But, alternatively to standard ceramic methods, only few examples of chemical methods for titanates preparation are known in literature.<sup>8-13</sup>

Our paper studies the possibility to obtain  $\text{MTiO}_3$  (M(II)= Co,Ni,Cu) by thermal decomposition of heterodinuclear complexes isolated in M(II)-Ti(IV)-oxime systems, where oxime is 1-phenyl -2(1'-piperidinyl) ethanone oxime (L), a ligand of the functionalized oxime type which contains not only the oxime group as a coordination site, but also an additional coordination site (piperidinyl) in  $\beta$  position to the oxime moiety.



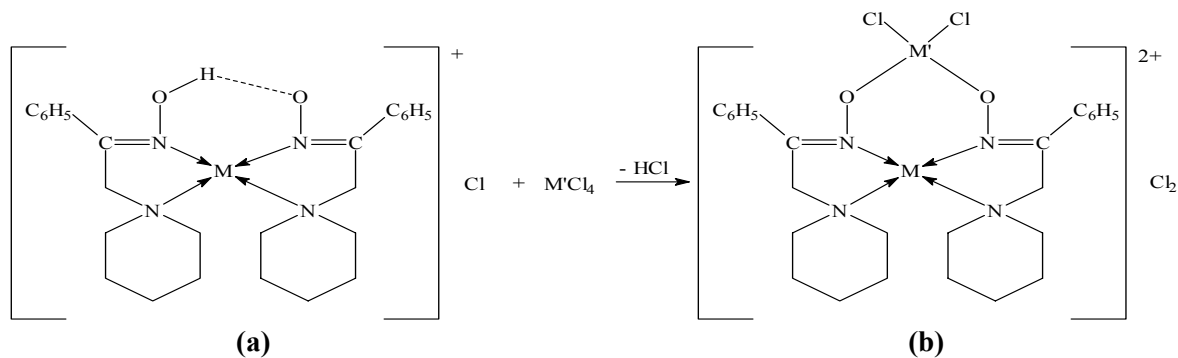
The chemistry of oxime/oximato metal complexes has been investigated since the beginning of the 20<sup>th</sup> century when the structure of Ni(II) dimethylglyoximate (the chelate five membered character of this complex) was recognized. The very rich chemistry of these species is due to a variety of coordination and reactivity modes like:

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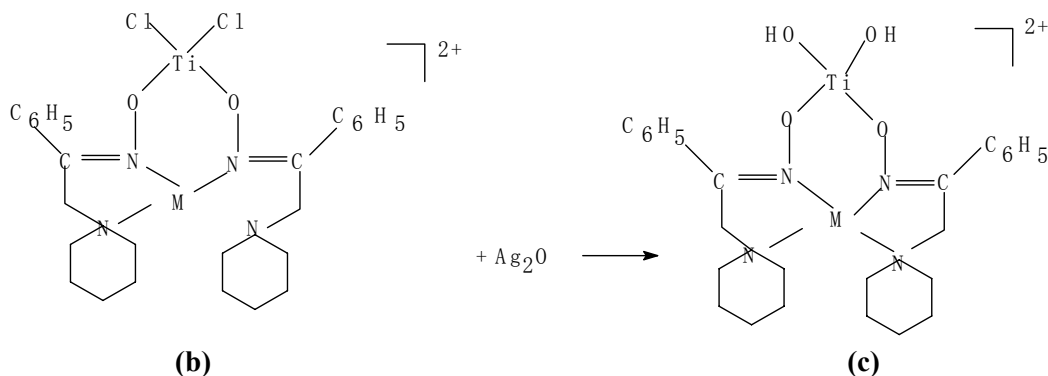


The oxime or oximate metal complexes have been extensively studied not only from the point of their traditional synthetic routes, structural aspects and analytical applications, but also for their high reactivity. Thus, the reactions of oxime species (like that of oxime OH group with Lewis acids) have been studied and a variety of clathrochelates (biscapped tris-dioximates) or semiclathrochelates

(monocapped tris-dioximates) of Fe(II,III), Co(II, III), Ni(II), Ru(II) with B, Si, Ge, Sn and Sb as a “cap” have been isolated and characterized.<sup>7,8</sup> These species differ from simple bis(o-dioxime) complexes by replacing the bridging hydrogen in the parent macrocycle by a bridging EX<sub>2</sub> group (E = B, Si, Sn, etc.; X = Cl, OH).



M = Co, Ni, Cu and M' = Ti



Such reactions are of greatest theoretical and practical interest (for example, models for dioxygen biological carriers). In the same time, such complexes could represent precursors for mixed oxides.

In this paper, titanates, MTiO<sub>3</sub> (M = Co, Ni, Cu) have been prepared in two stages: a) synthesis of [M(L-H)<sub>2</sub>Ti(OH)<sub>2</sub>](OH)<sub>2</sub> (M = Co, Ni, Cu) complex precursors; b) MTiO<sub>3</sub> preparation by thermal decomposition of the above precursors.

## RESULTS AND DISCUSSION

### Characterization of [M(L-H)<sub>2</sub>Ti(OH)<sub>2</sub>](OH)<sub>2</sub> complex precursors

The data of molar conductivities (10<sup>-3</sup>M in DMF solution) establish that [M(L-H)<sub>2</sub>Ti(OH)<sub>2</sub>](OH)<sub>2</sub> complexes are 1:2 electrolytes (see Table 1).

Table 1

Molar conductivity and bands in electronic spectra of the studied complexes

Complex	Color	Molar cond., $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ (Electrolyte type)	Bands (kK)	Assignment
[Co(L-H) <sub>2</sub> Ti(OH) <sub>2</sub> ](OH) <sub>2</sub> (1)	brown greenish	138,8 (1 : 2)	27.77 16.37 9.84	CT $^4A_2 \rightarrow ^4T_1(P)$ $^4A_2 \rightarrow ^4T_1(F)$
[Ni(L-H) <sub>2</sub> Ti(OH) <sub>2</sub> ](OH) <sub>2</sub> (2)	orange reddish	140.2 (1 : 2)	27.77 15.38	$^1A_{1g} \rightarrow ^1B_{2g}$ $^1A_{1g} \rightarrow ^1A_{2g}$
[Cu(L-H) <sub>2</sub> Ti(OH) <sub>2</sub> ](OH) <sub>2</sub> (3)	blue grenish	121.1 (1 : 2)	27.21 15.24 12.48 10.14	CT $z^2 \rightarrow x^2-y^2$ ( $a_{1g} \rightarrow b_{1g}$ ) $xz, yz \rightarrow x^2-y^2$ ( $e_g \rightarrow b_{1g}$ ) $xy \rightarrow x^2-y^2$ ( $b_{2g} \rightarrow b_{1g}$ )

The electronic spectra of all complexes are presented in Figure 1 and the assignment of the bands in Table 1.

The general aspect of the spectra indicates a very distorted tetrahedral configuration for Co(II) and Cu(II) complexes and a square planar geometry for Ni(II) complex.

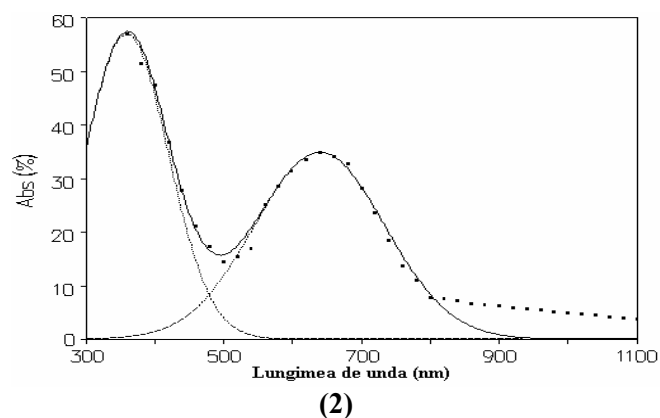
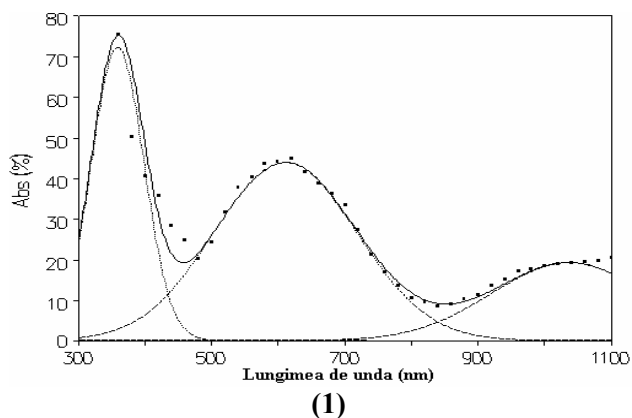
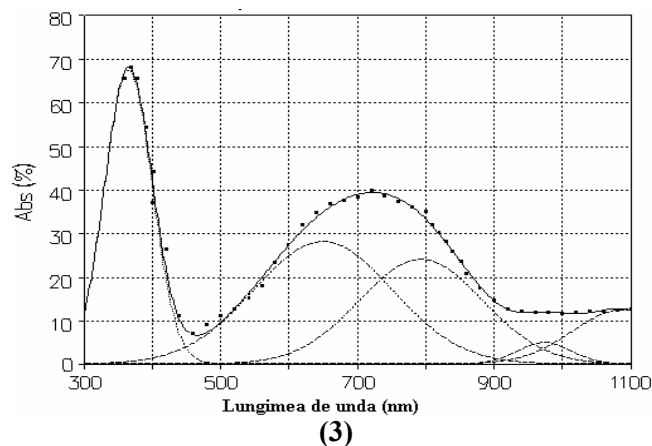


Fig. 1 – Electronic reflectance spectra of the studied complexes:

- (1) [Co(L-H)<sub>2</sub>Ti(OH)<sub>2</sub>](OH)<sub>2</sub>
- (2) [Ni(L-H)<sub>2</sub>Ti(OH)<sub>2</sub>](OH)<sub>2</sub>
- (3) [Cu(L-H)<sub>2</sub>Ti(OH)<sub>2</sub>](OH)<sub>2</sub>



These coordination geometries are also sustained by the determined values of molar magnetic susceptibilities of the complexes (Table 2), the

Co(II) and Cu(II) complexes being paramagnetic and Ni(II) complex diamagnetic.

Table 2

Magnetic data for the studied complexes

Complex precursor	Temperature, K	$\chi_{\text{exp}} \cdot 10^{-6}$ , $\text{cm}^3/\text{g}$	$\mu_{\text{eff}}$ , MB
(1)	293	10.8	3.036
(2)	293	0.24	0.958
(3)	293	10.75	3.227

The IR spectra have been recorded to confirm our supposition regarding the coordination mode of the ligand (L), the experimental data being assigned according to the literature.<sup>14</sup>

The data of IR spectra (Table 3) for complex precursors can be summarized as following: a) the absence of  $\nu_{\text{OH}}$  stretching vibration in the spectra of  $[\text{M}(\text{L-H})_2\text{Ti}(\text{OH})_2](\text{OH})_2$  is a proof of the deprotonation of the oxime ligand in these complexes; b) the characteristic  $\nu_{\text{CN}}^{\text{saturated cycle}}$  band from  $1310\text{ cm}^{-1}$  in the spectra of the free ligand is splitted and shifted to lower values in the spectra

of the complexes as a proof of ligand coordination through N piperidinyl; c) the  $\nu_{\text{C=N}}^{\text{exocycle}}$  band from  $1670\text{ cm}^{-1}$  in the spectrum of the free ligand is splitted and shifted to lower values in the spectra of complexes, indicating the ligand coordination through N of oxime group; d) in conclusion, the IR spectra of all complex precursors show characteristic bands positions, shifts and intensities which can be correlated to bidentate coordination of deprotonated ligand; e) the bending  $\text{Ti-O-H}$  frequency, present only in the spectra of complexes was found in  $1110\text{--}1120\text{ cm}^{-1}$  range.

Table 3

Characteristic frequencies ( $\text{cm}^{-1}$ ) in IR spectra of complex precursors

Complex precursor	$\nu_{\text{OH s}}$ $\nu_{\text{OH as}}$	$\nu_{\text{C=N}}$	$\delta_{\text{OH}}$	$\nu_{\text{CN cycle}}$	$\nu_{\text{N-O}}$	$\delta_{\text{Ti-O-H}}$
<b>L</b>	3450m, 3120m	1670s	1450i	1310i	950i, 980i	-
$[\text{Co}(\text{L-H})_2\text{Ti}(\text{OH})_2](\text{OH})_2$ <b>(1)</b>	-	1648s 1642s	-	1285i, 1310i	920i, 940i	1120
$[\text{Ni}(\text{L-H})_2\text{Ti}(\text{OH})_2](\text{OH})_2$ <b>(2)</b>	-	1640s 1660s	-	1285i, 1310i	920i, 940i	1125
$[\text{Cu}(\text{L-H})_2\text{Ti}(\text{OH})_2](\text{OH})_2$ <b>(3)</b>	-	1650s 1640s	-	1290i, 1310i	920i, 935i	1110

The thermal analysis of ligand (L) emphasizes a continuous losing of weight in a single step with a total decomposition at about  $350\text{--}400^\circ\text{C}$  (figure 2). The thermal curves of  $[\text{M}(\text{L-H})_2\text{Ti}(\text{OH})_2](\text{OH})_2$  ( $\text{M} = \text{Co}, \text{Ni}$ ) complexes (figure 3 and figure 4) are very similar; the processes of thermal decomposition of the complexes, oxidative degradation of the ligand and the formation of the mixed oxides phase take place in some overlapping steps between  $130\text{--}620^\circ\text{C}$  for  $\text{M} = \text{Co}$  and

$120\text{--}610^\circ\text{C}$  for  $\text{M} = \text{Ni}$ . The total weight loss corresponds to the  $\text{MTiO}_3$  formation that is also confirmed by XRD analysis of the thermal decomposition final products.

The thermal curves of  $[\text{Cu}(\text{L-H})_2\text{Ti}(\text{OH})_2](\text{OH})_2$  show two partial overlapping steps of complex decomposition with the formation of a mixed oxide at about  $600^\circ\text{C}$ .

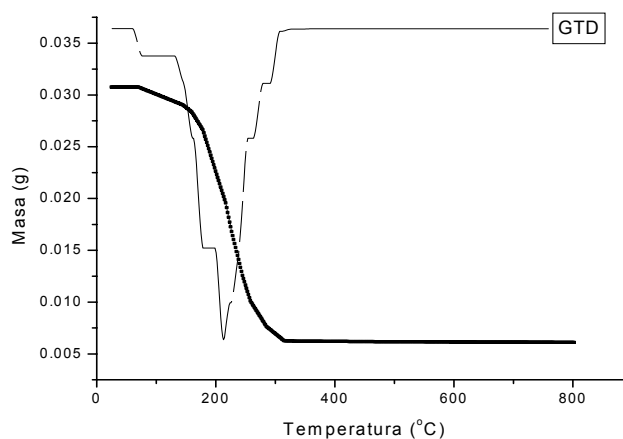


Fig. 2 – Thermal analysis (TG and DTG) of the ligand.

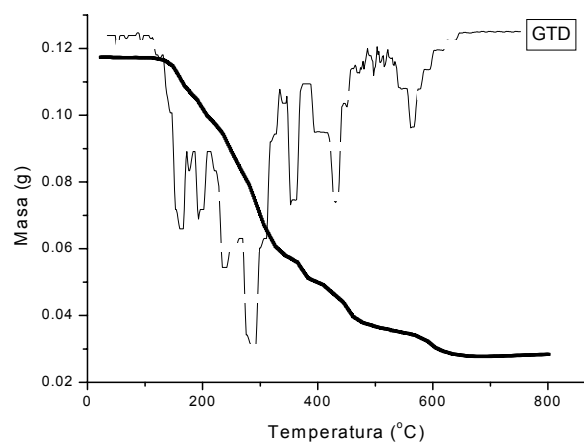


Fig. 3 – Thermal analysis (TG and DTG) of  $[\text{Co}(\text{L-H})_2\text{Ti}(\text{OH})_2](\text{OH})_2$ .

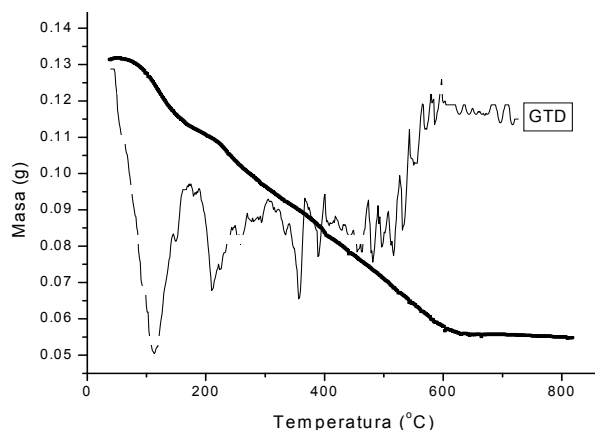


Fig. 4 – Thermal analysis (TG and DTG) of  $[\text{Ni}(\text{L-H})_2\text{Ti}(\text{OH})_2](\text{OH})_2$ .

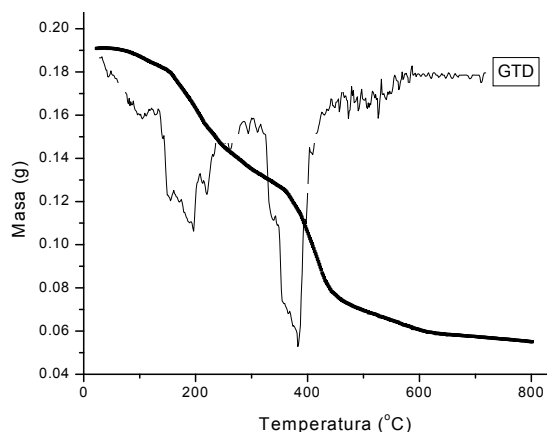


Fig. 5 – Thermal analysis (TG and DTG) of  $[\text{Cu}(\text{L-H})_2\text{Ti}(\text{OH})_2](\text{OH})_2$ .

A structural formulae of semiclathrocholate type (c) has been proposed for the studied complexes on the basis of all physico-chemical data obtained.

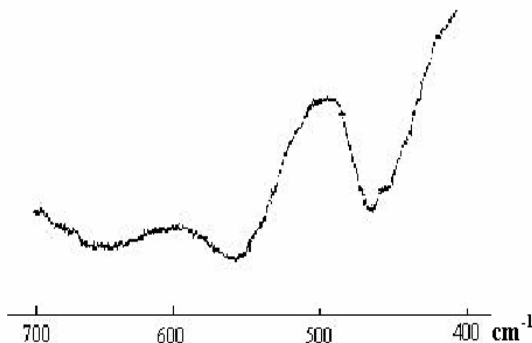
### Characterization of titanates

The thermal analyses (TG-DTG) of the complex precursors showed the formation of the mixed oxides at about of 600°C.

For example, the formation of nickel titanate by calcination of precursor at 650°C, a half hour was also supported by IR spectrum (figure 6) and XRD data (figure 7, table 3).

IR spectrum in 400-700  $\text{cm}^{-1}$  range of the mixed oxide sample present a splitted large band at 450 – 465  $\text{cm}^{-1}$  characteristic to Ni – O bond and another large band at 550  $\text{cm}^{-1}$  assigned as Ti-O band.

Fig. 6 – IR spectrum of  $\text{NiTiO}_3$ .



The XRD data presented in Figure 7 sustain the ilmenite structure of  $\text{NiTiO}_3$  prepared by the calcination of  $[\text{Ni}(\text{L-H})_2\text{Ti}(\text{OH})_2](\text{OH})_2$  complex precursor.

A good concordance of XRD pattern for  $\text{NiTiO}_3$  obtained in this study with that of ilmenite  $\text{FeTiO}_3$  is observed from the data presented in Table 4.

Titanates are important materials for many industrial applications such as pigments, catalysts, resistors or other electronic devices. For this reason, the electrical conductivity,  $\sigma$  ( $\Omega^{-1}\text{cm}^{-1}$ ) and its variation with temperature of  $\text{NiTiO}_3$  prepared was also determined in this study.

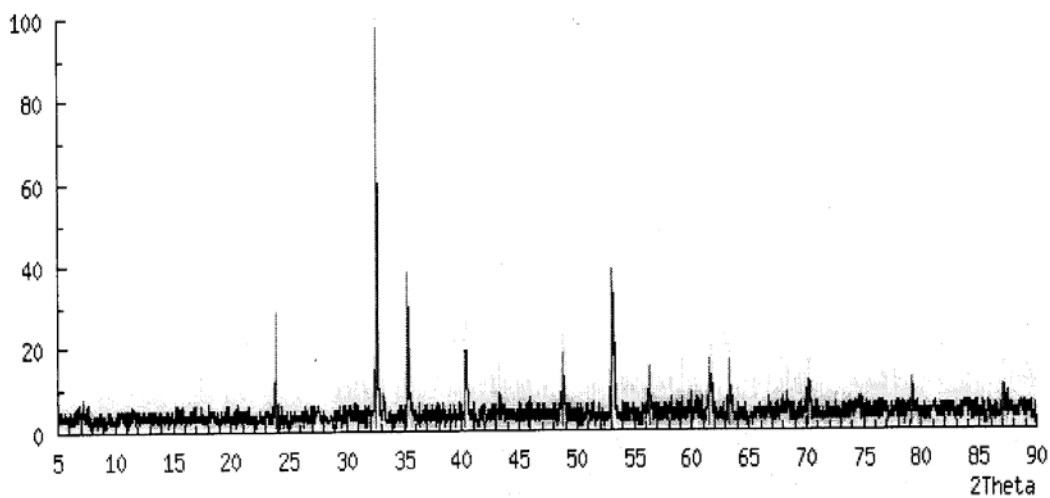
The electrical conductivity was carried out using a two probe method over a temperature range 25-800°C. The values of electrical conductivity  $\sigma$ , between  $10^{-4}$  –  $10^{-8}$   $\text{mho cm}^{-1}$  and a general increasing with temperature indicate the dielectric property of nickel titanate (figure 8).

Conductivity  $\sigma$  presents a general linear increasing following an Arrhenius behaviour: between 60-100°C conductivity does not change much with temperature, but after 120°C, the value of  $\sigma$  increases up to 800°C. The plateau observed after this temperature could be assigned to a structural transition ilmenite-perovskite that is indicated in literature.

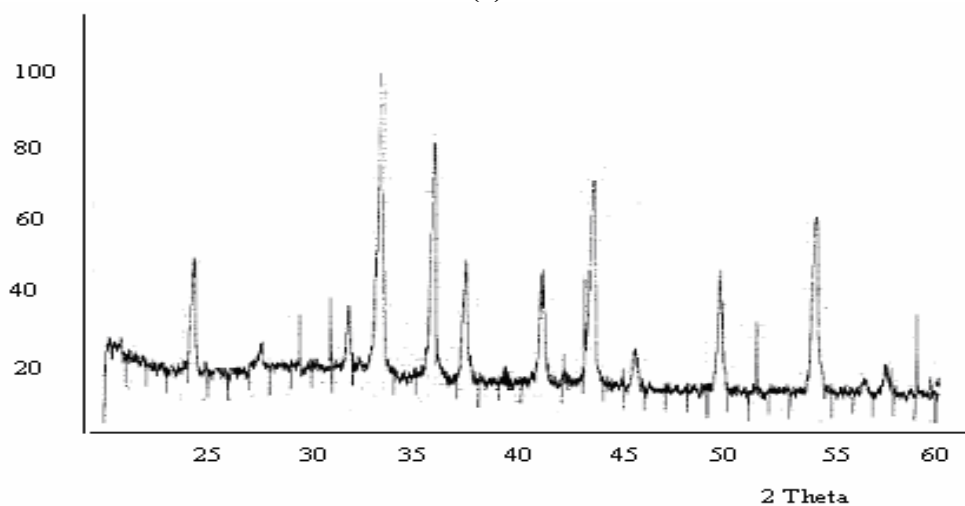
Table 4

Characteristic XRD interferences of NiTiO<sub>3</sub> obtained in this paper and that of FeTiO<sub>3</sub> (ilmenite)

NiTiO <sub>3</sub>			FeTiO <sub>3</sub> (ASTM)		
$\theta$	d	I <sub>r</sub>	$\theta$	d	I <sub>r</sub>
12.45	3.57	50	12.70	3.50	65
15.95	2.80	35	15.90	2.80	15
16.35	2.70	100	16.25	2.75	100
18.00	2.49	80	18.40	2.44	75
18.70	2.40	40	18.70	2.40	20
20.50	2.19	35	20.80	2.21	23
21.65	2.08	70	21.00	2.05	40
24.75	1.83	40	24.50	1.85	30
27.00	1.69	65	27.00	1.69	35
29.90	1.54	35	29.90	1.54	50



(a)

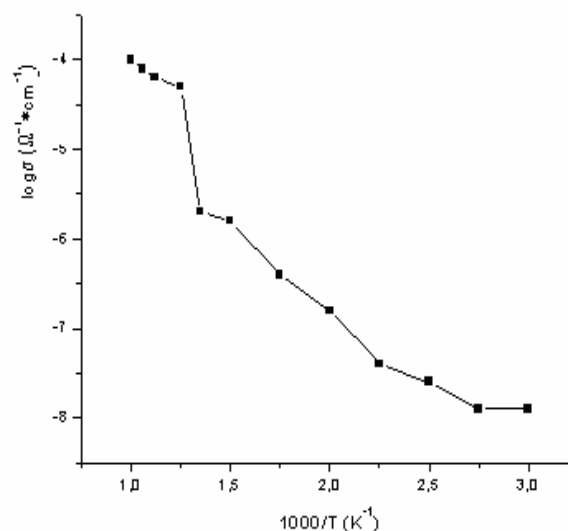


(b)

Fig. 7 – XRD pattern of NiTiO<sub>3</sub> obtained in this study by the calcination 30 minutes of [Ni(L-H)<sub>2</sub>Ti(OH)<sub>2</sub>](OH)<sub>2</sub> complex precursor at:

- (a) 650<sup>o</sup>C  
(b) 700<sup>o</sup>C

Fig. 8 – Electrical conductivity vs temperature behaviour for NiTiO<sub>3</sub> prepared from complex precursor.



## EXPERIMENTAL

### Ligand synthesis

Ligand 1-phenyl-2-(1'-piperidiny)ethanone oxime (L) has been prepared from the corresponding β-aminoketone on treatment with NH<sub>2</sub>OH·HCl in CH<sub>3</sub>OH as solvent in the presence of NaOH.<sup>15</sup>

### Synthesis of [M (L-H)<sub>2</sub>TiCl<sub>2</sub>]Cl<sub>2</sub> (M=Co, Ni, Cu) complexes

Complexes have been synthesized by refluxing of a methanol solution of [ML(L-H)]Cl prepared elsewhere<sup>16</sup> and TiCl<sub>4</sub> in molar ratio 1: 2 up to the color changes from dark green to light green for copper complex and from brown-green to orange for nickel complex.

After two hours of boiling, solid products (green for copper, brown for cobalt and orange for nickel) were filtered, washed with methanol and dried in a desiccator over P<sub>4</sub>O<sub>10</sub>.

Found for CoTiC<sub>26</sub>H<sub>34</sub>N<sub>4</sub>O<sub>4</sub>Cl<sub>4</sub>: Co%, 8.30; Ti%, 7.35; N%, 4.41; Cl%, 21.10

Calc. Co%, 8.66; Ti%, 7.05; N%, 4.11; Cl%, 20.85

Found for NiTiC<sub>26</sub>H<sub>34</sub>N<sub>4</sub>O<sub>4</sub>Cl<sub>4</sub>: Ni%, 8.25; Ti%, 7.30; N%, 4.30; Cl%, 21.03

Calc. Ni%, 8.65; Ti%, 7.05; N%, 4.21; Cl%, 20.83

Found for CuTiC<sub>26</sub>H<sub>34</sub>N<sub>4</sub>O<sub>4</sub>Cl<sub>4</sub>: Cu%, 9.10; Ti%, 7.45; N%, 4.50; Cl%, 21.03

Calc. Cu%, 9.26; Ti%, 7.00; N%, 4.08; Cl%, 20.71

### Synthesis of [M (L-H)<sub>2</sub>Ti (OH)<sub>2</sub>] (OH)<sub>2</sub> (M=Co, Ni, Cu) complexes

A mixture formed by [M(L-H)<sub>2</sub>TiCl<sub>2</sub>]Cl<sub>2</sub> and wet silver oxide in 1 : 4 molar ratio has been boiled in reflux about 3 hours. After the filtration of AgCl, the solution has been evaporated in air; the solid separated products were filtered, washed with methanol, ether and dried in a desiccator over P<sub>4</sub>O<sub>10</sub>.

Found for: CoTiC<sub>26</sub>H<sub>38</sub>N<sub>4</sub>O<sub>8</sub>: Co%, 9.10; Ti%, 7.90; N%, 4.61

Calc. Co%, 9.22; Ti%, 7.45; N%, 4.50

Found for: NiTiC<sub>26</sub>H<sub>38</sub>N<sub>4</sub>O<sub>8</sub>: Ni%, 9.10; Ti%, 7.90; N%, 4.60

Calc. Ni%, 9.80; Ti%, 7.55; N%, 4.20

Found for: CuTiC<sub>26</sub>H<sub>38</sub>N<sub>4</sub>O<sub>8</sub>: Cu%, 9.80; Ti%, 7.46; N%, 4.90

Calc. Cu%, 10.35; Ti%, 7.82; N%, 4.56

### Synthesis of MTiO<sub>3</sub> titanates (M=Co, Ni, Cu)

Fresh prepared [M(L-H)<sub>2</sub>Ti(OH)<sub>2</sub>](OH)<sub>2</sub> (M = Co, Ni, Cu) complex precursors have been calcinated at different temperatures (650°C, 700°C, 800°C), 30 minutes when powders of titanates were obtained.

*Molar electrical conductivities* have been recorded in DMF solutions at 25°C with a OK 102/1 Radelkis Conductometer having a 0.1 – 0.5 S measuring range.

*IR spectra* have been recorded with a Perkin-Elmer spectrophotometer using KBr pellets at reference in the 400-4000 cm<sup>-1</sup> range.

*Electronic reflectance spectra* were recorded using a Specord M 40 Carl Zeiss Jena with MgO as standard.

*Magnetic measurements* were carried out using a Faraday balance at room temperature with Mohr salt as standard.

*XRD patterns* have been recorded with a Phillips diffractometer P.W. 1140 using CuK<sub>α</sub> radiation.

*TG-DTG curves* have been carried out on a digital thermobalance with thermoregulator vertical oven coupling with PC acquisition

*Electrical conductivities* have been performed using a two probe method over 25-800°C temperature range. The sample holder consisted of two stainless steel electrodes, each having a thickness of 2 cm and an area of 3 cm<sup>2</sup>. A d.c. voltage of 1.5 V was passed through the sample and the corresponding current was measured with an electrometer; the temperature of the samples were measured with a calibrated chromel-alumel thermocouple.

## CONCLUSION

The paper describes the synthesis of MTiO<sub>3</sub> by the calcination of [M(L-H)<sub>2</sub>Ti(OH)<sub>2</sub>](OH)<sub>2</sub>

complex precursors, at only 650°C, 30 minutes. Titanates obtained by this route are pure, high crystallized material with ilmenite structure. NiTiO<sub>3</sub> obtained is a dielectric material.

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