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SYNTHESIS OF CALCIUM METANIOBATE BY THERMAL DECOMPOSITION OF A COPRECIPITATION PRODUCT

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Abstract

The paper presents a new, nonconventional method, based upon coprecipitation, for the synthesis of niobium oxidic compounds. The coprecipitation product of niobic acid with calcium oxalate was used as precursor. Calcium metaniobate was obtained by appropriate thermal treatment of the coprecipitate. The coprecipitation mechanism was studied and the optimal conditions for quantitative precipitation of niobium and calcium were established. The mechanism of thermal decomposition of the coprecipitate was investigated by means of differential thermal analysis and X-ray powder diagrams. The final product of thermal decomposition, calcium metaniobate, is formed at 730°C.

Keywords: calcium metaniobate, DTA mechanism of thermal decomposition, synthesis, X-ray powder diagrams

Introduction

Oxidic compounds are usually obtained by ceramic methods, i.e. solid-state reactions, starting from metal oxides or carbonates. The main drawbacks of these conventional methods are: high temperatures, long reaction times, difficulties in obtaining a reaction product of high homogeneity, poor control of the composition and imperfect reproducibility.

The 'nonconventional', chemical methods used in recent years avoid some of these disadvantages. These methods ensure the molecular homogeneity of the products, well-established stoichiometry and good reproducibility. The high reactivity of the chemical precursors permits lower reaction temperatures and shorter reaction times.

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This paper continues the presentation of our results on the preparation of niobium oxidic compounds by nonconventional methods [1–5] based upon coprecipitation.

The literature contains a few reports on the synthesis of niobates by nonconventional methods [6–9]. So far, calcium metaniobate has not been obtained by such a method.

Results and discussion

Mechanism of coprecipitation in the oxotrioxalatoniobic acid – calcium nitrate – ammonium hydroxide system,

$H_3[NbO(C_2O_4)_3]$–$Ca(NO_3)_2$–NH_4OH

Two components of the system investigated were coprecipitated as niobic acid and calcium oxalate. The coprecipitation was carried out in a system containing oxotrioxalatoniobic acid (with an excess of oxalic acid) and calcium nitrate, with a Nb:Ca ratio of 2:1, using ammonium hydroxide as coprecipitation reagent. The system was investigated in order to establish the optimal conditions for quantitative coprecipitation of niobium and calcium. For this purpose, the equilibrium in the oxotrioxalatoniobic acid – calcium nitrate – ammonium hydroxide system was studied by potentiometric and analytical methods.

The *pH* variation in the $H_3[NbO(C_2O_4)_3]$–$Ca(NO_3)_2$–NH_4OH–$H_2C_2O_4$ system was controlled by potentiometry, as a function of NH_4OH concentration. The concentration of NH_4OH was expressed by the ratio

$$R=\frac{[NH_4OH]}{[Ca(NO_3)_2]+[NbO(C_2O_4)_3]^{3-}}$$

The *pH* variation curves as a function of *R* for the system, and also for the individual components of the system, are illustrated in Fig. 1.

Curve 1 shows the *pH* variation in the $[NbO(C_2O_4)_3]^{3-}$–$H_2C_2O_4$–NH_4OH system (individual component: niobium) and exhibits two changes: the first, between *pH* 3 and 5, indicating the precipitation of niobium as niobic acid, and the second, between *pH* 5.5 and 7.5, due to the neutralization of oxalic acid, overlapping with the neutralization of oxotrioxalatoniobic acid.

Curve 2 represents the *pH* variation in the $Ca(NO_3)_2$–$H_2C_2O_4$–NH_4OH system (individual component: calcium) and exhibits only one pronounced jump between *pH* 3.2 and 7.5, due exclusively to the neutralization of oxalic acid, with equivalence point at *pH* 6.7.

Curve 3, for the complex system containing niobium and calcium, exhibits two changes. The first, between *pH* 3.0 and 4.5 (less pronounced) with an inflexion point at *pH* 3.5, is due to the overlap of the two precipitation reactions occurring in the system: the precipitation of calcium oxalate, which begins at *pH* 0.52:

$$Ca(NO_3)_2 + H_2C_2O_4 + NH_4OH \rightleftharpoons CaC_2O_4 + 2\,H_2O$$

and the precipitation of niobic acid, beginning at *pH* 3:

$$2\,H_3[Nb(C_2O_4)_3] + nH_2O + 12\,NH_4OH \rightleftharpoons Nb_2O_5 \cdot nH_2O + 6\,(NH_4)_2C_2O_4$$

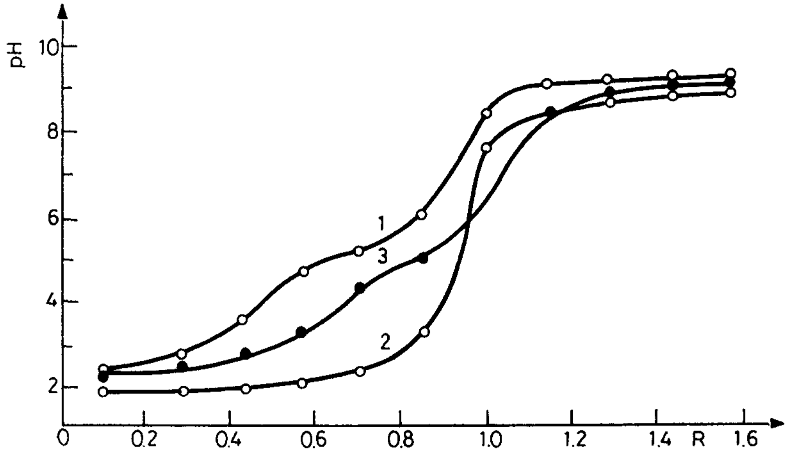

Fig. 1 The *pH* variation in the systems: 1) Nb-ox–$H_2C_2O_4$; 2) $Ca(NO_3)_2$–$H_2C_2O_4$ 3) Nb-ox–$Ca(NO_3)_2$– $H_2C_2O_4$ Nb-ox = $H_3[NbO(C_2O_4)_3]$

The second jump in the potentiometric curve is due to neutralization of the oxalic acid excess, corresponding to the equivalence point at *pH* 6.75. It partly overlaps with the end of the neutralization of oxotrioxalatoniobic acid, accompanied by the precipitation of niobic acid.

Table 1

Ca^{2+}	$H_2C_2O_4$	pH_i	pH_f	$pH_{equiv.H_2C_2O_4}$
$5.3 \cdot 10^{-2}$ M	$1.6 \cdot 10^{-1}$ M	–0.52	0.53	6.75

Table 1 shows the *pH* values calculated for the beginning (pH_i) and end (pH_f) of the precipitation, and also the *pH* at the equivalence point of oxalic acid.

The precipitation of calcium oxalate and niobic acid is complete at *pH* 7. The quantitative coprecipitation was confirmed by quantitative chemical analysis.

It should be mentioned that the precipitation of calcium hydroxide in this system is out of the question, because the solubility of calcium oxalate ($K_{sp}=2.3\cdot10^{-9}$) is much lower than that of calcium hydroxide ($K_{sp}=5.5\cdot10^{-6}$) and the precipitation of calcium hydorxyde begins, at the concentration used, at a much higher *pH*, which is not reached in this system.

Formation of calcium metaniobate by thermal decomposition of the coprecipitate

The thermal decomposition of the niobic acid – calcium oxalate coprecipitate was investigated by means of thermogravimetry, differential thermal analy-

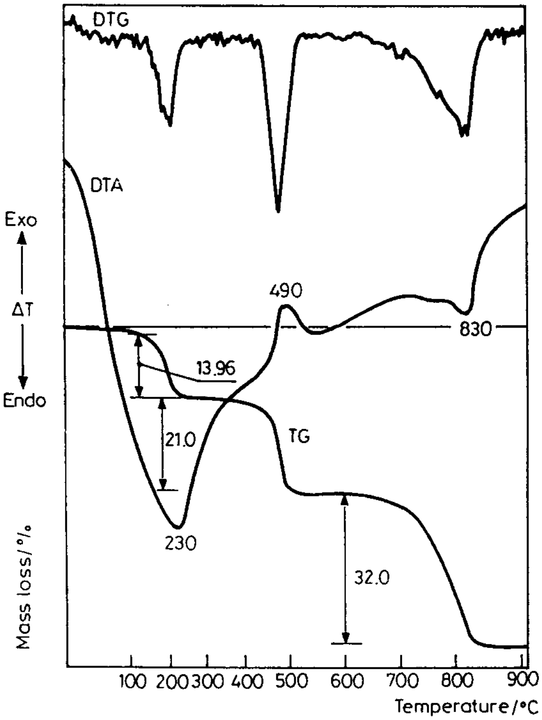

Fig. 2 TG and DTA curves of $CaC_2O_4\cdot H_2O$

sis, the IR spectra and X-ray diffraction powder diagrams. For comparison, the TG and DTA curves for pure calcium oxalate were recorded; they are in agreement with literature reports on the thermal decomposition of divalent metal oxalates [10].

From the TG and DTA curves of $CaC_2O_4\cdot H_2O$ (Fig. 2), it is obvious that calcium oxalate eliminates the crystallization water in the temperature interval 140–240°C; this is associated with a pronounced endothermic effect at 240°C.

The second weight loss (420–490°C) is assigned to the decomposition of CaC_2O_4 to $CaCO_3$ and CO. As the runs are performed in air, the CO is oxidized simultaneously to CO_2. Since the exothermic effect of CO oxidation is higher than the endothermic effect of thermal decomposition of CaC_2O_4, the overall effect at 490°C is exothermic.

Table 2 Thermal decomposition of the niobic acid–calcium oxalate coprecipitate

Temperature / °C	Mass loss / %	Species loss	Thermal effect / °C		Compounds
			Endo	Exo	
					$CaC_2O_4\cdot H_2O$
20–230	13.0	H_2O	230		CaC_2O_4
230–490	21.0	CO		490	$CaCO_3\cdot xCO_2\cdot yCO$
490–830	32.0	CO_2	830		CaO
					$Nb_2O_5\cdot nH_2O$ + $CaC_2O_4\cdot xH_2O$
20–180	13.96	$6H_2O$	180		Nb_2O_5 + CaC_2O_4
180–320	14.10		260		
320–420	3.14	CO		420	Nb_2O_5 + $CaCO_3\cdot xCO_2\cdot yCO$
420-505	5.23	CO_2		505	
505–700	7.32			675	
700–1000	1.04	CO_2		730	$CaNb2O_6\cdot xCO_2\cdot yCO$
					$CaNb_2O_6$

In fact, there is some disagreement in the literature about concernes the oxidation of CO to CO_2 in the thermal decomposition of simple and complex oxalates [10–12]. Chromatographic analysis of the gaseous products demonstrated the presence of a mixture of CO and CO_2. The gaseous products remain partially adsorbed on the solid phase and the desorption occurs stepwise with increasing temperature [13].

The endothermic effect at 830°C, accompanied by a loss in mass of one mole of CO_2, corresponds to the decomposition of calcium carbonate to calcium oxide.

A scheme for the thermal decomposition of the coprecipitate and for that of pure calcium oxalate has been established on the basis of the TG and DTA data, and is given in Table 2. Figure 3 illustrates the TG and DTA curves for the coprecipitate.

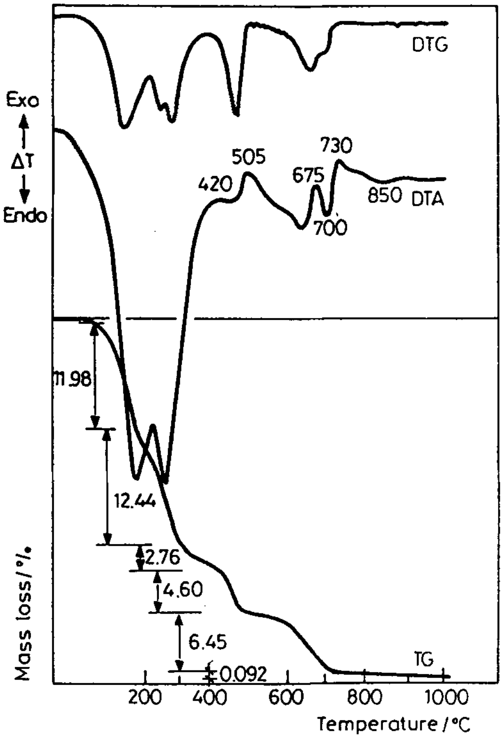

Fig. 3 TG and DTA curves of the coprecipitate

The loss of crystallization water is marked by two endothermic effects, at 180 and 260°C. The weight loss in this interval corresponds to 6 H_2O molecules. The weight loss in the interval 320–505°C is assigned to the decomposition of CaC_2O_4 to $CaCO_3$ and CO, the latter being directly oxidized to CO_2. This fact explains the exothermic effects (420 and 505°C) which accompany CaC_2O_4 decomposition.

The reaction between niobic acid and calcium carbonate to yield calcium metaniobate is marked by a double exothermic effect at 675 and 730°C. The resulting CO_2 is eliminated stepwise, as indicated by the weight loss in the TG curve. It shows that CO_2 is partially adsorbed on the solid phase.

Table 3 Infrared spectra (cm^{-1})

CaC_2O_4	Coprecipitate	$CaNb_2O_6$	Assignment
520	515		δ(O–C=O)
670	(600)		
		650	ν(Nb–O)
785	773		δ(O–C=O)
1315	1313		ν(CO), δ(O–C=O)
1370	1395		
1385			
1620	1620		ν(C=O), (H_2O)
1650	1660		

The final product of thermal decomposition of the niobic acid – calcium oxalate coprecipitate is calcium metaniobate, formed at 730°C. This was confirmed by X-ray powder diffraction diagrams (by comparison) and IR spectra.

The IR spectra of the coprecipitate, and of calcium oxalate and calcium niobate, are presented in Table 3. The IR spectrum of the coprecipitate exhibits the characteristic bands of the oxalate anion. These bands are not present in the spectrum of the thermal decomposition product, which shows only a single band, characteristic of niobates, at 650 cm^{-1}.

Table 4 X-Ray powder diffraction lines of the coprecipitation product (CuK_α radiation)

$CaC_2O_4\cdot xH_2O$+niobic acid		$CaC_2O_4\cdot 2H_2O$ [14] ASTM 17-541		$CaC_2O_4\cdot H_2O$ [14] ASTM 20-231	
d / Å	*I*/*I*$_0$	*d* / Å	*I*/*I*$_0$	*d* / Å	*I*/*I*$_0$
6.1920	100	6.18	100		
5.9131	82			5.93	100
5.7815	38			5.79	30
4.4108	38	4.42	30		
3.9287	38	3.91	8		
3.6437	82	3.68	12	3.68	12
2.9712	44			2.966	45
2.7481	100	2.775	65		
2.3522	44	2.342	4	2.355	30
2.2431	38	2.2431	25		

Table 5 X-Ray powder diffraction lines of the thermal decomposition product (CuK_α radiation)

$CaNb_2O_6$ (after DTA)		$CaNb_2O_6$ ASTM 31-289 [14]	
d / Å	*I*/*I*$_o$	*d* / Å	*I*/*I*$_o$
7.4668	17	7.44	40
5.3857	7	5.35	10
3.9339	10		
3.7339	23	3.74	30
3.4357	9	3.43	20
3.2009	3		
3.1163	3		
3.0558	100	3.02	100
2.9565	4		
2.8760	10	2.87	20
2.7912	6		
2.7076	5	2.69	10
2.6795	4		
2.6052	9	2.61	20
2.5660	3	2.57	10
2.5211	7	2.515	20
2.4880	6	2.494	20
2.3072	2	2.311	10
2.2467	4	2.246	10
2.1486	3	2.145	10
2.0968	2	2.088	10
1.9769	5	1.968	10
1.9325	7	1.932	20

The X-ray powder diagram of the initial coprecipitate is given in Table 4, and that of the thermal decomposition product in Table 5.

As suggested by the data in Table 4, the initial coprecipitate is a mixture of calcium oxalate mono- and dihydrates, while the niobic acid, being amorphous, does not show up in the X-ray powder diagram.

The X-ray powder diagram of the thermal decomposition product (Table 5) indicates the formation of $CaNb_2O_6$, with a structure similar to that mentioned in the literature [14]. Some additional lines of weak intensity, which could not be identified, are also observed; these may belong to a Nb_2O_5 modification, incompletely reacted in the process. Some small differences in the values of *d* (Å) and I/I_o relative to the ASTM file can be explained by the procedure used for preparing $CaNb_2O_6$, i.e. the nonisothermal conditions, which prevented the perfect ordering of the structure.

Experimental

Solutions of oxalatoniobic acid and calcium nitrate of preestablished concentrations were prepared in volumetric flasks.

The oxalatoniobic acid solutions were obtained by dissolving freshly prepared niobic acid in an excess of oxalic acid, corresponding to a $Nb:H_2C_2O_4$ ratio of 1:5; the excess of oxalic acid was necessary to ensure the stability of the solution on storage and to avoid the precipitation of niobic acid.

The accurate amount of niobium in the stock solution was established by gravimetric (mass) analysis.

The calcium nitrate solution was obtained by dissolving the appropriate amount of calcium carbonate in the stoichiometric amount of nitric acid and adding water to the mark in a volumetric flask.

The concentrations used were:

$$C_{Ca(NO_3)_2} = 5.3\cdot 10^{-2}\ M$$

$$C_{Nb-ox} = 10.6\cdot 10^{-2}\ M$$

These values were chosen so that mixing of equal volumes of the solutions containing niobium and calcium would afford a mole ratio of 2 Nb: 1 Ca.

The coprecipitation was achieved by mixing equal volumes of the oxalatoniobic acid and calcium nitrate solutions, and adding determined volumes of 0.1 *M* ammonium hydroxide solution, according to potentiometric analysis data.

The coprecipitate was filtered off, washed with water, dried at 105°C, and subjected to thermal decomposition at 800°C for calcium niobate formation.

For chemical analysis of the coprecipitate, niobium and calcium were determined gravimetrically and oxalate by permanganometric titration.

The infrared spectra were recorded in KBr pellets on a Carl Zeiss UR-20 spectrophotometer, in the range 4000–400 cm^{-1}.

The X-ray powder diagrams were recorded with a TUR-M 62 diffractometer, using CuK_α radiation.

The TG and DTA curves were recorded with a Paulik-Paulik-Erdey MOM derivatograph, in air, at a heating rate of 5 $deg\cdot min^{-1}$.

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Zusammenfassung — Es wird eine neue unübliche, auf Mitfällung beruhende Methode zur Darstellung von oxidischen Niobverbindungen vorgestellt. Dabei wird das Kopräzipitat von Niobsäure mit Calciumoxalat als Präkursor verwendet. Durch eine entsprechende Wärmebehandlung des Kopräzipitates erhält man Calciummetaniobat. Der Mechanismus der Mitfällung wurde untersucht und die optimalen Bedingungen für eine quantitative Fällung von Niob und Calcium ermittelt. Mit Hilfe von DTA und Debye-Scherrer-Aufnahmen wurde der Mechanismus der thermischen Zersetzung des Kopräzipitates untersucht. Das Endprodukt der thermischen Zersetzung, Calciummetaniobat, wird bei 730°C gebildet.