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SYNTHESIS OF LEAD METANIOBATE BY THERMAL DECOMPOSITION OF A COPRECIPITATION PRODUCT

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Abstract

The paper reports a new, nonconventional method for the preparation of oxygen-containing niobium compounds, based upon coprecipitation. The coprecipitation product of niobic acid with lead oxalate was used as precursor. Lead metaniobate was obtained by proper thermal treatment of the coprecipitate. The coprecipitate mechanism was studied and the optimal conditions for quantitative precipitation of niobium and lead were established. The mechanism of thermal decomposition of the coprecipitate was investigated by differential thermal analysis and X-ray powder diagrams. The final product of thermal decomposition, lead metaniobate, is formed at 850°C.

Keywords: oxygen-containing niobium compounds, lead metaniobate, TG and DTA, X-ray

Introduction

Nonconventional methods – also called "chemical methods" – are widely used as practical methods for preparing oxygen-containing compounds. These procedures have some advantages over conventional methods – based exclusively on solid state reactions – as follows:

- homogeneity at molecular level
- well defined stoichiometry
- higher reactivity of the chemical precursors
- higher dispersion degree
- lower temperatures of reactions (lower energy consumption)
- higher reaction rates
- shorter thermal treatments
- formation of higher density materials (after appropriate thermal treatment).

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The chemical precursors can be coprecipitation products, complex (coordination) compounds, metal–organic compounds, etc. The methods used for obtaining these precursors are sometimes more complicated than simple solid state reactions, but these difficulties are compensated by the advantages mentioned above.

This paper continues our preoccupation for the synthesis of niobium oxidic compounds with ferroelectric properties by nonconventional methods [1–5].

Previously, only few attempts to prepare niobium compounds by nonconventional methods were reported [6–8]. This is especially true for lead metaniobate [9].

The synthesis of lead metaniobate (a compound with good ferroelectric properties) by solid state reactions, involves some difficulties because of the relatively high volatility of lead oxide. The solid state reaction needs temperatures above 1000°C and under these conditions lead oxide can be volatilized, therefore the composition of the final product may be nonreproducible. This deficiency is avoided by the chemical method of coprecipitation. This method uses lead oxalate and niobic acid as chemical precursors, which need much lower temperatures for the formation of lead metaniobate.

Results and discussion

The mechanism of coprecipitation in the oxotrioxalatoniobic acid – lead nitrate–ammonium hydroxide: $H_3[NbO(C_2O_4)_3]$–$Pb(NO_3)_2$–NH_4OH *system*

The method of oxalate coprecipitation was used for obtaining lead metaniobate. Lead and niobium were coprecipitated as lead oxalate, respectively niobic acid, in ammonium hydroxide medium. The initial solution for the coprecipitation contained lead oxalate and oxotrioxalatoniobic acid, and the coprecipitation agent was ammonium hydroxide.

The equilibria which prevail in this system were studied by potentiometric and other analytical methods and the optimal conditions for the quantitative coprecipitation were established.

Each component (lead and niobium) was studied separately, by potentiometric titration, as well as the binary system containing both components. The variation of pH was followed as a function of ammonium hydroxide concentration, expressed by the ratio R:

$$R = \frac{[NH_4OH]}{[Nb\text{–}Ox + [Pb(NO_3)_2]} \qquad Nb\text{–}Ox = H_3[NbO(C_2O_4)_3]$$

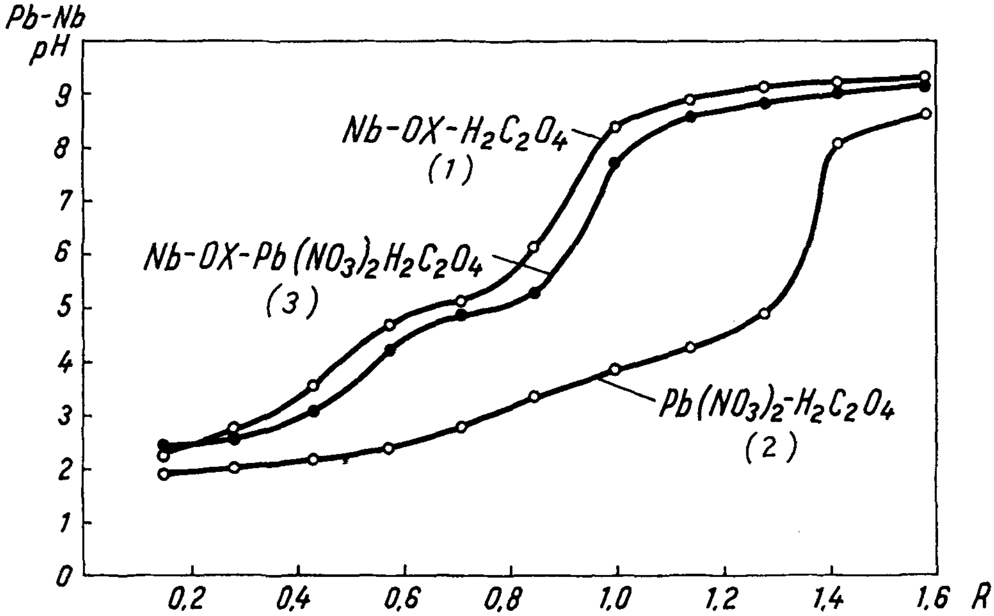

Fig. 1 Potentiometric study of the system Pb(II)–Nb(V)–$H_2C_2O_4$–NH_4OH

Figure 1 illustrates the curves of *pH* variation for the separate components (curves 1 and 2) and for the binary system (curve 3).

Curve 1 shows the *pH* variation in the Nb–Ox, i.e. $H_2C_2O_4$–NH_4OH system, and exhibits three changes: a slow one at *pH* 3–5 which is due to niobic acid precipitation, quite complete at *pH* 5.5; a second change, between *pH* 6.5 and 7.5 due to oxalic acid neutralization; this latter one overlaps with the neutralization of oxotrioxalatoniobic acid.

The equilibria which occur in this system are as follows:

$$Pb(NO_3)_2 + H_2C_2O_4 + 2NH_4O \rightleftharpoons PbC_2O_4 + 2NH_4NO_3 + 2H_2O$$

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

These equilibria are entirely shifted to the right at $pH > 7$.

Table 1 Conditions of precipitation of PbC_2O_4

$C_{Pb^{2+}}$	$C_{H_2C_2O_4}$	pH_i	pH_f	$p_{equiv.\ H_2C_2O_4}$
$5.3{\cdot}10^{-2}$ M	$1.6{\cdot}10^{-1}$ M	–0.5	0.7	6.75

The *pH* values calculated for the precipitation of Pb^{2+} as lead oxalate (for the beginning pH_i and the end pH_f at the concentrations used experimentally, are presented in Table 1.

The conclusion of the potentiometric study is that the quantitative coprecipitation of lead and niobium takes place at *pH* 7. This fact was confirmed by the chemical analysis of the solutions after filtration of the coprecipitate. These solutions were free of Pb^{2+} and niobium (by spectrographic analysis).

Table 2 X-ray powder diffraction lines

Pb–Nb–oxalate coprecipitate (lines of PbC_2O_4)*		$PbNb_2O_6$ ** (after DTA)	
d / Å	*I* / %	*d* / Å	*I* / %
		7.1366	5
		5.2233	13
4.8264	80	4.8670	3
4.5568	85		
4.2601	65		
4.1853	65		
3.7498	85		
3.3919	100		
3.2993	70		
3.2569	40	3.2022	3
		3.1090	100
		3.0316	92
		2.9435	2
		2.7869	4
		2.6367	5
		2.6152	5
		2.3708	2
		2.2217	3
2.0906	50	2.1569	25
2.0046	40	2.0448	3
		1.9756	2
		1.9108	8
		1.8625	5
		1.8047	4

* ASTM 14-803 **ASTM 20-589

The values calculated for the solubility of lead oxalate and lead hydroxide demonstrate that under the conditions used, the precipitation of lead hydroxide cannot take place.

Formation of lead niobate by the thermal decomposition of the coprecipitate

The coprecipitate lead oxalate–niobic acid was studied by differential thermal analysis, X-ray diffraction and IR spectra, as well as the product of the thermal decomposition of the coprecipitate. The X-ray diffraction lines (Table 2) for the coprecipitate indicate a well crystallized product, with characteristic diffraction lines of lead oxalate (ASTM 14-830) [10].

The infrared spectra (Table 3) of the coprecipitate show the presence of characteristic oxalato group lines.

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

PbC_2O_4	Pb–Nb–oxalate coprecipitate	$PbNb_2O_6$	Assignation
510	580		δ(O–C=O)
530		650	ν(Nb–O)
780	775		δ(O–C=O)
790			
1290	1280		
1315	1300		ν(C–O), δ(O–C=O)
1370	1370		
1385	1385		
1570			
1605	1600		ν(C=O) (H_2O)
1640	1610		
	3380		(H_2O)
	3440		

The X-ray diffraction pattern of the thermal decomposition product (ca. 900°C) exhibits the characteristic diffraction lines of lead metaniobate, well crystallized (ASTM 20-589) [10].

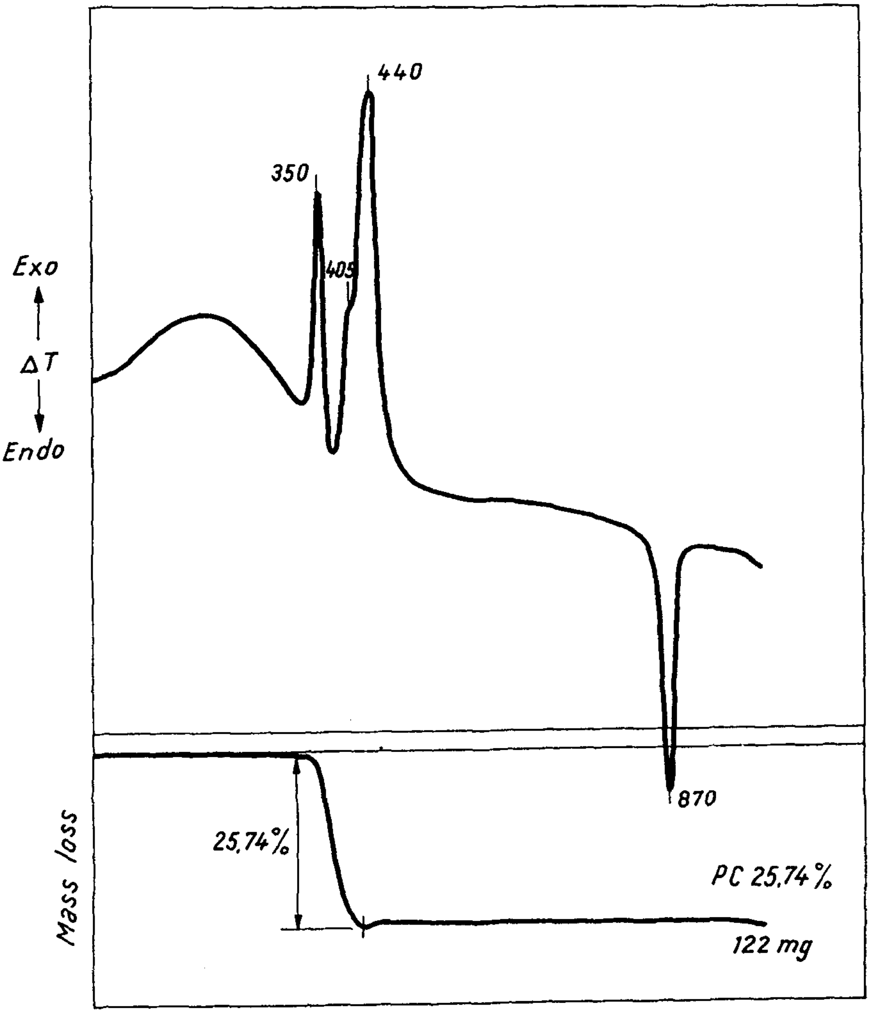

Fig. 2 DTA/TG curves of PbC_2O_4

The infrared spectra of the thermal decomposition product show that all lines of the oxalato group disappeared and only the Nb–O line at ca. 650 cm^{-1} is present.

These facts indicate that the thermal decomposition product of the coprecipitate lead oxalate–niobic acid is undoubtedly lead metaniobate $PbNb_2O_6$.

The mechanism of the thermal decomposition of the coprecipitate was studied on the basis of the thermogravimetric and differential thermal analysis data, as well as the X-ray diffraction data and infrared spectra.

Table 4 Thermal decomposition of the niobic acid–lead oxalate coprecipitate

Temperature range /°C	Data of TG curves		DTA peak / °C		Compounds
	Mass loss / %	Species lost	Endothermal	Exothermal	
Lead oxalate (pure) PbC_2O_4					
20–350				350	$PbCO_3 \cdot xCO_2$
350–440	25.74	CO		405	Formation of PbO
		CO_2		440	
			870		Melting of PbO
Coprecipitate $Nb_2O_5 \cdot nH_2O + PbC_2O_4$					
20–150	6.00	$2H_2O$	150		$Nb_2O_5 + PbC_2O_4$
150–322	5.28	CO		322	
322–380	1.92	$(1-x)CO_2$		380	$Nb_2O_5 + PbCO_3 \cdot xCO_2$ ads.
380–535	2.40			535	$PbNb_2O_6 \cdot xCO_2$
535–1000	1.20	xCO_2 ads.		850	$PbNb_2O_6$

The scheme of the suggested mechanism of the thermal decomposition is presented in Table 4, and the TG and DTA curves for the coprecipitate in Fig. 3. The TG and DTA curves for PbC_2O_4 are given in Fig. 2.

The DTA curve of PbC_2O_4 exhibits two pronounced exothermal effects: one at 350°C which corresponds to the beginning of the thermal decomposition of lead oxalate with formation of lead carbonate, accompanied by an important weight loss between 350–405°C, the elimination of a CO molecule. The second exothermal effect at 440°C indicates the formation of PbO, with loss of a CO_2 molecule. The total weight loss up to 440°C corresponds to the elimination of $CO+CO_2$.The endothermal effect at 870°C is due to the melting of PbO.

The DTA curve of the coprecipitate (Fig. 3) exhibits the first endothermal effects at 150°C, accompanied by a weight loss of 6%, which corresponds to the loss of two molecules of water of crystallization. The two following exothermal effects at 322 and 380°C accompany the decomposition of lead oxalate and the formation of lead carbonate, with elimination of a CO molecule. The carbon monoxide formed in this reaction is partially oxidised to carbon dioxide, which

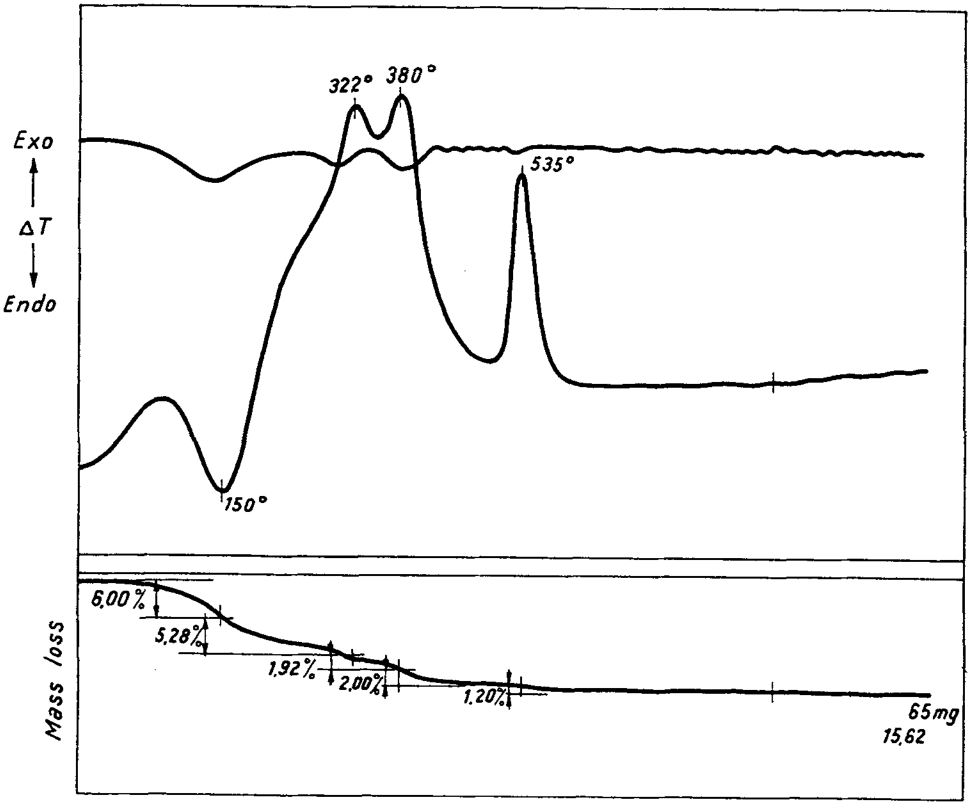

Fig 3 DTA/TG curves of coprecipitate

remains partially adsorbed in the solid product, and is gradually eliminated from it. The exothermal effect at 535°C marks the reaction between lead carbonate and niobium pentoxide with formation of lead metaniobate. The weak exothermal effect at 850°C can be assigned to a recrystallization of lead metaniobate.

Experimental

Solutions of preestablished concentrations of oxalatoniobic acid and lead nitrate 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 in order to ensure the stability of the solution on storage and to avoid precipitation of niobic acid. The exact amount of niobium in solution was established by gravimetric analysis.

The coprecipitation was achieved by mixing equal volumes of the oxalatoniobic acid and lead nitrate solutions and adding determined volumes of 0.1 mol/l ammonium hydroxide solution, according to potentiometric data. The coprecipitate was filtered, washed with water and dried at 105°C, then subjected to thermal decomposition for lead niobate formation.

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 TURM-M 62 diffractometer, using CuKα radiation. The TG and DTA curves were recorded with a Paulik-Paulik-Erdey MOM Derivatograph, in air, at a heating rate of 5 deg·min^{-1}.

References

1 L. Marta, M. Zaharescu and C. G. Macarovici, Rev. Roum. Chim., 24 (1979) 1115.
2 L. Marta, M. Zaharescu and C. G. Macarovici, Rev. Roum. Chim., 27 (1982) 82.
3 L. Marta, M. Zaharescu and I. Haiduc, Rev. Roum. Chim., 28 (1983) 957.
4 L. Marta, M. Zaharescu and C. G. Macarovici, J. Thermal Anal., 26 (1983) 87.
5 L. Marta, M. Zaharescu, I. Haiduc and C. G. Macarovici, J. Thermal Anal., 28 (1983) 175.
6 V. A. Titova, I. F. Cherednichenko and N. G. Kisel, Zhur. Neorg. Khim., 12 (1967) 1457.
7 R. C. Mehrotra, M. M. Agraval and P. N. Kapoor, J. Chem. Soc., (1968) 2073.
8 G. Daendliker and H. Morawietz, Decomposition of Organometallic Compounds, Refractory Ceramics, Metals, Metal Alloys, Proc. Int. Symp., 1967 (Publ. 1968).
9 I. V. Filatov, A. N. Grinberg, I. I. Kovalevskaya and L. Ya. Filatov, Zhur. Neorg. Khim., 22 (1977) 2054.
10 Inorganic Index to the Powder Diffraction File, ASTM, Philadelphia, 1967.

Zusammenfassung — Vorliegend wird eine neue, unkonventionelle, auf Kopräzipitation beruhende Darstellung von sauerstoffhaltigen Niobverbindungen beschrieben. Das Kopräzipitationsprodukt von Niobsäure mit Bleioxalat wurde als Präkursor verwendet. Bei entsprechender thermischer Behandlung des Kopräzipitates erhält man Bleimetaniobat. Der Kopräzipitationsmechanismus wurde untersucht und die optimalen Bedingungen für eine quantitative Fällung von Niob und Blei ermittelt. Der Mechanismus der thermischen Zersetzung des Kopräzipitates wurde mittels DTA und Debye-Scherrer-Aufnahmen untersucht. Das Endprodukt der thermischen Zersetzung, Bleimetaniobat, wird bei 850°C gebildet.