

THERMAL SYNTHESIS OF BARIUM AND BARIUM–STRONTIUM METANIOBATES BY USING A COPRECIPITATION METHOD

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The paper presents a new, non-traditional method for the synthesis of barium metaniobate, BaNb_2O_6 , and of a mixed barium–strontium metaniobate, $\text{Ba}_{0.29}\text{Sr}_{0.71}\text{Nb}_2\text{O}_6$, through the thermal decomposition of coprecipitation products. The conditions of quantitative precipitation of the metals as niobic acid and barium or barium–strontium oxalate were established. The mechanism of thermal decomposition of the coprecipitate was deduced from differential thermal analysis and X-ray diffraction data. Barium metaniobate forms at 470°C , below the temperature required in the synthesis based upon the solid-state reaction between Nb_2O_5 and BaCO_3 (1100°C). The mixed barium–strontium compound is formed at 700°C , below the 1100°C used in the reaction between Nb_2O_5 , BaCO_3 and SrCO_3 .

In recent years much attention has been paid to the preparation of oxide systems by non-traditional methods, which avoid some of the defects of the usual ceramic methods, such as high temperatures and prolonged reaction times. Among these non-traditional methods, coprecipitation has already been used for some oxidic systems, its main features being rapidity and simplicity. However, it has been very little used for oxide systems containing niobium [1, 2], although the synthesis of such systems by solid-state reaction presents many difficulties.

In a previous paper [3] we reported the synthesis of strontium metaniobate by the thermal decomposition of some coprecipitation products. In the present work we have used the method to prepare barium metaniobate and a mixed barium–strontium niobate of the type $\text{Ba}_x\text{Sr}_{1-x}\text{Nb}_2\text{O}_6$.

Results and discussion

Coprecipitation in the system oxotrioxalatonibic acid – barium nitrate – ammonium hydroxide

The coprecipitation of niobium with barium or with barium and strontium was achieved in a system containing oxotrioxalatonibic acid (with an excess of oxalic acid) and barium nitrate or a mixture of barium and strontium nitrates, with a con-

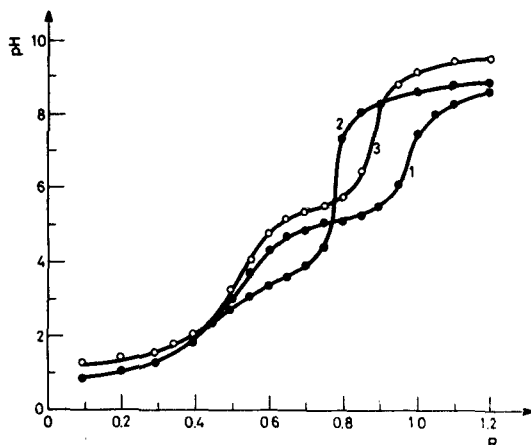


Fig. 1 pH variation in the systems: 1 - Nb-ox - $H_2C_2O_4$, 2 - $Ba(NO_3)_2$ - $H_2C_2O_4$, 3 - Nb-ox - $Ba(NO_3)_2$ - $H_2C_2O_4$

stant Nb:Ba ratio of 2:1 or a Nb:Na:Sr ratio of 2:0.29:0.71, in the presence of ammonium hydroxide as precipitating agent. This system was studied by potentiometric and analytical methods, to establish the optimum conditions for the quantitative coprecipitation of the metals.

The pH variation in the system $H_3[NbO(C_2O_4)_3]-Ba(NO_3)_2-H_2C_2O_4-NH_4OH$ was followed by potentiometry, as a function of the NH_4OH concentration. The concentration of NH_4OH is expressed by the ratio

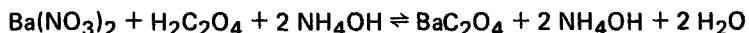
$$R = \frac{[NH_4OH]}{[Ba(NO_3)_2] + [Nb - ox]}$$

where Nb - ox = $H_3[NbO(C_2O_4)_3]$. The curve of the pH variation in the system is shown in Fig. 1 (curve 3), together with the curves of the separate components of the system: curve 1 shows the pH variation in the system Nb - ox - $H_2C_2O_4 - NH_4OH$ (containing only niobium), and curve 2 the pH variation in the system $Ba(NO_3)_2 - H_2C_2O_4 - NH_4OH$ (containing only barium).

Curve 1 exhibits two changes: the first one, between pH 3 and 5, corresponding to the precipitation of niobium as niobic acid, and the second, more pronounced, between pH 5.5 and 7.8, due to the neutralization of oxalic acid, overlapping with the neutralization of oxotrioxalatonioic acid.

In the barium-containing system (curve 2) the pH jump between pH 4.5 and 7.5 is due exclusively to the neutralization of oxalic acid, with the equivalence point at pH 6.75.

Curve 3, for the complex system containing niobium and barium, exhibits two pH changes: a jump between pH 2.0 and 4.8 with an inflexion point at pH 3.5, due to the overlapping of the two precipitation reactions occurring in the system, *viz.*: the precipitation of barium oxalate, which begins at pH 2.4:



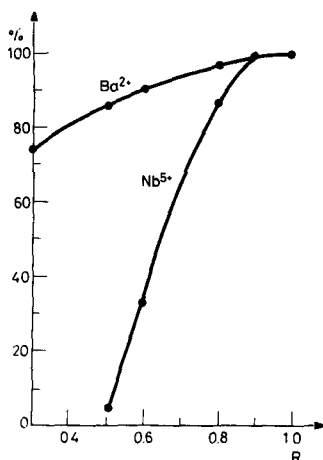
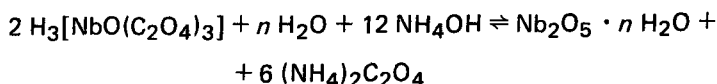


Fig. 2 Variation of coprecipitation degree of Nb^{5+} and Ba^{2+} as a function of ratio R

and the precipitation of niobic acid, beginning at $\text{pH} \sim 3$, according to the equation:



The barium oxalate precipitation is complete at $\text{pH} 7$, as is that of niobic acid.

The second jump in curve 3, between $\text{pH} 5.8$ and 8.3 , is due, as in the first two systems, to the neutralization of oxalic acid excess, and partly overlaps with the end of the neutralization of oxotrioxalatonioic acid, accompanied by the precipitation of niobic acid.

The pH values calculated for the initial and final stages of the precipitation, at definite concentrations of Ba^{2+} and $\text{C}_2\text{O}_4^{2-}$, and the pH at the equivalence point of oxalic acid, are given in Table 1.

The degree of coprecipitation of Nb^{5+} and Ba^{2+} from the system has been determined by quantitative analysis of the precipitates obtained at different pH values.

The coprecipitation degrees of barium and niobium, expressed as percentages, as a function of the NH_4OH concentration (expressed as the ratio R) and of the pH conditions, are shown in Figs 2 and 3, respectively. The potentiometric data are confirmed by the quantitative analysis.

Table 1 pH values for given reaction conditions

$C_{\text{Ba}^{2+}}$	$C_{\text{C}_2\text{O}_4^{2-}}$	pH_i	pH_f	$\text{pH}_{\text{eq. H}_2\text{C}_2\text{O}_4}$
$3.06 \cdot 10^{-2} \text{M}$	$2.98 \cdot 10^{-1} \text{M}$	0.90	3.21	6.75

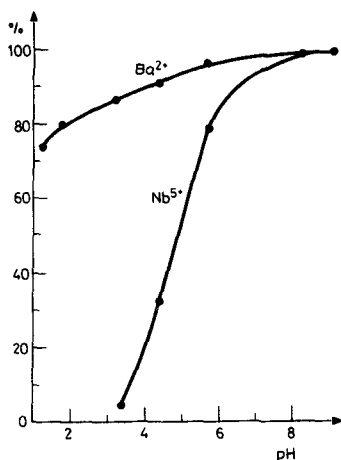


Fig. 3 Variation of coprecipitation degree of Nb^{5+} and Ba^{2+} as a function of pH

At low pH ($\text{pH} = 2.4$) the precipitation of barium oxalate takes place. This is the only component present in the precipitates formed up to $\text{pH} \approx 3$. At this value niobic acid precipitation begins. The precipitation of barium oxalate is practically complete at $\text{pH} = 8$, and that of niobic acid at $\text{pH} = 7.5$. These values are confirmed by the potentiometric curves.

The alternative of barium hydroxide precipitation, in addition to or instead of barium oxalate, can be disregarded under these conditions, on the basis of both experimental and calculated data. Thus, barium hydroxide precipitation begins at $\text{pH} = 13$ at the given concentration of Ba^{2+} ; this value is not reached in our system. In addition, the solubility of barium oxalate ($K_{\text{sp}} = 1.1 \times 10^{-7}$) is much lower than that of the hydroxide ($K_{\text{sp}} = 5 \times 10^{-3}$); therefore, the hydroxide cannot precipitate in a system containing oxalate ions.

The chemical analysis of the precipitate also demonstrates the presence of barium oxalate in the expected amount.

Coprecipitation in the system $\text{H}_3[\text{NbO}(\text{C}_2\text{O}_4)_3] - \text{Ba}(\text{NO}_3)_2 - \text{Sr}(\text{NO}_3)_2 - \text{H}_2\text{C}_2\text{O}_4 - \text{NH}_4\text{OH}$

For the synthesis of the mixed metaniobate $\text{Ba}_{0.29}\text{Sr}_{0.71}\text{Nb}_2\text{O}_6$, also known under the trade name "banastron", which has remarkable electrical properties [4–7], the coprecipitation in the system containing Nb, Ba and Sr in the appropriate ratio was investigated. The coprecipitation was carried out under the same conditions as in the previously-described Ba–Nb system.

The potentiometric curves shown in Fig. 4 give the pH variation in the ammonium hydroxide titration of the systems containing each metal separately (curve 1 – Nb, curve 2 – Sr, curve 3 – Ba), or in the complex Nb–Ba–Sr mixture (curve 4). The

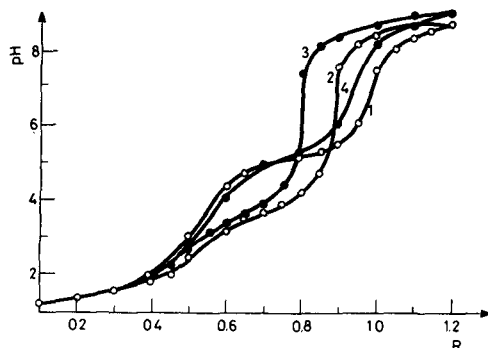


Fig. 4 pH variation in the systems: 1 - Nb-ox - $\text{H}_2\text{C}_2\text{O}_4$, 2 - $\text{Sr}(\text{NO}_3)_2$ - $\text{H}_2\text{C}_2\text{O}_4$, 3 - $\text{Ba}(\text{NO}_3)_2$ - $\text{H}_2\text{C}_2\text{O}_4$, 4 - Nb-ox - $\text{Sr}(\text{NO}_3)_2$ - $\text{Ba}(\text{NO}_3)_2$ - $\text{H}_2\text{C}_2\text{O}_4$

ammonium hydroxide concentration is expressed by the value of R , which for curve 4 can be written as:

$$R = \frac{[\text{NH}_4\text{OH}]}{[\text{Nb-ox}] + [\text{Sr}(\text{NO}_3)_2] + [\text{Ba}(\text{NO}_3)_2]}$$

Curve 4, describing the three-component Nb-Ba-Sr system, is similar to those of the binary Nb-Ba and Nb-Sr systems.

In the three-component system, the following three precipitation reactions occur simultaneously:

- precipitation of strontium oxalate, beginning at $\text{pH} = 2$, which is complete at $\text{pH} = 7$;
- precipitation of barium oxalate, beginning at $\text{pH} = 2.4$, which is complete at $\text{pH} = 8.0$;
- precipitation of niobic acid, beginning at $\text{pH} = 3$, which is quantitative at $\text{pH} = 7$.

The first part of the potentiometric curve 4, between $\text{pH} 2.5$ and 4.5 , is due to the overlapping of the three precipitation equilibria. The second potential jump, between $\text{pH} 5.8$ and 8.2 , is due to the neutralization of oxalic acid present in the system, having an equivalent point at $\text{pH} 6.75$. Quantitative precipitation in the ternary Nb-Ba-Sr system (in the preestablished ratio 2 Nb:0.29 Ba:0.71 Sr) is achieved at $\text{pH} 8.5$.

The coprecipitates obtained in the Nb-Ba and Nb-Ba-Sr systems were characterized by chemical analysis and infrared spectra, and were subjected to thermal analysis.

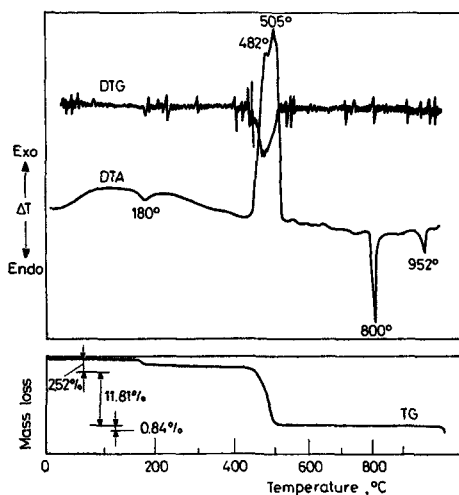


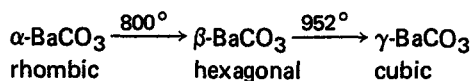
Fig. 5 TG and DTA curves of barium oxalate

Thermal decomposition of niobic acid – barium oxalate coprecipitate

The coprecipitate containing hydrated niobic acid and barium oxalate was subjected to thermal analysis in order to establish the conditions of formation of barium metaniobate. For comparison, TG and DTA curves of pure barium oxalate were also recorded (Fig. 5). The latter were in agreement with published literature data [6, 7].

The loss of crystallization water is associated with the exothermic effect at 180°, and corresponds to a content of 0.5 H₂O for each mole of BaC₂O₄. The decomposition of BaC₂O₄ occurs at ca. 500° and is associated with the strongly exothermic effects at 482° and 505°. These are probably explained by overlapping with the endothermic effect of BaCO₃ formation. The weight loss shown by the TG curve occurs rapidly at 440–515° and corresponds to an almost complete elimination of a carbon monoxide molecule. Between 514–1000° only minor weight loss is observed, corresponding to elimination of gaseous products absorbed onto the solid phase. The carbon monoxide formed initially is probably partially oxidized to carbon dioxide.

The DTA curve shows two endothermic effects, at 800° and 952°, associated with polymorphic transformations of barium carbonate, in agreement with literature data [8]:



The thermal decomposition of the niobic acid – barium oxalate coprecipitate is illustrated by the TG and DTA curves shown in Fig. 6, in agreement with the scheme given in Table 2. The shapes of the curves for the precipitate are quite different from

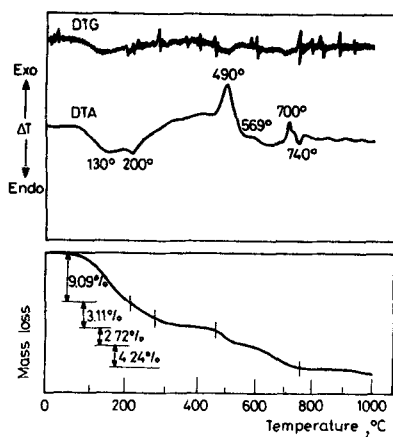


Fig. 6 TG and DTA curves of niobic acid – barium oxalate coprecipitate

Table 2 Thermal analysis data for BaC_2O_4 and niobic acid – barium oxalate coprecipitate

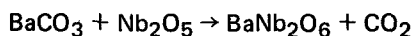
temperature, °C	Weight loss (TG)		Thermal effects, °C		Compounds
	% loss	lost species	endo	exo	
20–180	1.26				$\text{BaC}_2\text{O}_4 \cdot 0.5 \text{H}_2\text{O}$
180–440	1.26	$0.5 \text{H}_2\text{O}$	180		BaC_2O_4
440–515	11.81			482	$\text{BaCO}_3 \cdot x\text{CO}_2\text{ads.}$
515–1000	0.84	CO		505	$\text{BaCO}_3 (\alpha)$
			800		$\text{BaCO}_3 (\beta)$
			952		
20–200	9.09	$3 \text{H}_2\text{O}$	130		$\text{Nb}_2\text{O}_5 \cdot x\text{H}_2\text{O} + \text{BaC}_2\text{O}_4 \cdot 0.5 \text{H}_2\text{O}$
200–450	5.11		200		$\text{Nb}_2\text{O}_5 + \text{BaC}_2\text{O}_4$
450–569	2.72	$\text{CO},$ $(1-x)\text{CO}_2$		490	$\text{Nb}_2\text{O}_5 + \text{BaCO}_3 \cdot x\text{CO}_2\text{ads.}$
569–740	4.24			569	$\text{BaNb}_2\text{O}_6 \cdot x\text{CO}_2$
				700	
740–1000	0.60	$x\text{CO}_2$	740		BaNb_2O_6 orthorhombic

Table 3 Infrared spectra for the Ba–Nb system

BaC ₂ O ₄ · 0.5 H ₂ O cm ⁻¹	Coprecipitate cm ⁻¹	BaNb ₂ O ₆ cm ⁻¹	Assignment
490 s			$\nu(\text{C}-\text{C})$
	530 vw, br		$\delta(\text{O}-\text{C}=\text{O})$
660 m		650 w, br	$\nu(\text{Nb}-\text{O})$ —niobate
725 w			
760 w	780 vw		$\delta(\text{O}-\text{C}=\text{O})$
840 vs	860 vw, br		$\nu(\text{C}-\text{C}), \nu(\text{C}-\text{O})$
1030 m			
1230 s			
1315 s	1320 m		$\nu(\text{C}-\text{O}), \delta(\text{O}-\text{C}=\text{O})$
	1440 v		$\nu(\text{C}-\text{O}), \nu(\text{C}=\text{C})$
1640 s, br	1630 m, br		$\nu(\text{C}=\text{O}), (\text{H}_2\text{O})$

those for pure barium oxalate. In the case of strontium, investigated earlier [3], the curves were very similar, suggesting that the coprecipitate contained a simple physical mixture of SrC₂O₄ and niobic acid. In the case of barium it can be assumed that barium oxalate and niobic acid reacted to form a mixed compound. This is in agreement with the infrared spectral data and the X-ray diffraction diagram. Thus, the infrared spectrum of the coprecipitate (Table 3) shows only three of the characteristic bands of the free oxalate, and these are much attenuated. The X-ray diffraction diagram (Table 4) of the coprecipitate is completely unlike that of pure barium oxalate. The mixed compound is predominantly amorphous. Only a few lines are observed, suggesting that amorphous niobic acid penetrates the barium oxalate lattice, to form a mixed barium–niobium compound of low crystallinity, not identified before.

The thermal decomposition of the mixed coprecipitate described above begins with loss of water, occurring stepwise up to 200°; the total weight loss corresponds to 3 H₂O molecules. Their elimination is accompanied by two endothermic effects, at 130° and 200°. This is followed by the decomposition of barium oxalate, marked by an exothermic effect at 490°. The weight loss associated with this reaction, due to the elimination of CO, partially oxidized to CO₂, occurs slowly and stepwise, in agreement with the reactions:



The gaseous products are partially retained in the solid phase, and the desorption occurs gradually up to 1000°.

The reaction between barium carbonate and niobic acid, with formation of barium metaniobate, is evidenced by the exothermic effect at 700°.

Table 4 X-ray diffraction lines of BaC₂O₄ and Ba–Nb coprecipitate

BaC ₂ O ₄		Ba–Nb coprecipitate	
<i>d</i> , Å	<i>hkl</i> ₀	<i>d</i> , Å	<i>hkl</i> ₀
8.4249	8	8.2833	43
5.0390	8	7.7753	76
4.6707	5	7.5249	33
4.4394	3	7.1151	23
4.3322	6	6.8730	23
4.0953	6	6.4260	30
3.7951	3	5.0791	20
3.5900	100	5.0276	26
3.2503	7	4.7958	36
3.1688	15	4.7550	36
3.1168	14	4.5567	20
3.0582	5	3.9171	20
2.9554	3	3.7823	26
2.9066	3	3.7200	36
2.7336	9	3.3987	43
2.5383	7	3.2433	16
2.3312	9	3.2090	26
2.2347	3	3.1534	100
2.1992	3	3.0644	26
2.1550	7	3.0587	26
2.0950	3	2.6175	66
2.0641	3	2.2357	23
2.0077	4	2.1222	36
1.8214	4	2.0776	23

Table 5 X-ray diffraction lines of Ba–Nb coprecipitate formed at 700°C

<i>d</i> , Å	<i>hkl</i> ₀	<i>d</i> , Å	<i>hkl</i> ₀
4.2183	25	3.3022	25
4.1140	25	3.1339	40
3.9515	40	3.0339	30
2.7354	100	2.9980	35
3.6420	40	2.9177	55
3.3386	30	—	—

The X-ray powder diagram of the product formed at 700° suggests the formation at this temperature of an intermediate compound, probably having a bronze-type structure and a low degree of crystallinity, whose diffraction lines have not been indexed so far (Table 5).

The DTA curve exhibits an endothermic effect at 740°, corresponding to a polymorphic transformation of barium metaniobate, from the metastable to the

Table 6 X-ray diffraction lines of BaNb₂O₆

$d, \text{Å}$	I/I_0	$d, \text{Å}$	I/I_0
3.9584	20	2.1472	16
3.9342	20	2.0978	6
3.4716	16	1.9827	20
3.3094	10	1.9673	23
3.2364	39	1.8690	7
3.1404	100	1.8476	10
3.0359	63	1.8059	7
2.9824	75	1.7699	18
2.9478	24	1.7498	28
2.7968	50	1.7103	8
2.6187	10	1.6905	5
2.5218	12	1.6802	3
2.3678	8	1.6600	11
2.2736	10	1.6540	12
2.1839	16	1.6426	20
2.1531	17	1.6156	12

orthorhombic modification. This temperature of formation of orthorhombic barium metaniobate is significantly lower than the value reported in the literature, i.e. 1100° [9, 10], for its formation in a solid-state reaction between niobium pentoxide and barium carbonate. This suggests that the reactivity of the mixed compound formed by coprecipitation is much higher than that of mechanical mixtures in the solid state. The transformation of this product into barium niobate on heating is even more favoured than its formation by thermal decomposition of the oxalatonioium complex [11].

The X-ray powder diffraction diagram of the thermal decomposition product of the coprecipitate (mixed compound) clearly confirms the formation of orthorhombic barium metaniobate, with a well-formed crystalline structure [12] (Table 6).

Thermal decomposition of the niobic acid – strontium oxalate – barium oxalate coprecipitate

The scheme of the thermal decomposition of the Ba–Sr–Nb coprecipitate, established on the basis of the TG and DTA curves (Fig. 7), is shown in Table 7.

The shapes of the TG and DTA curves of the ternary system coprecipitate are very close to those of the Ba–Nb system. The thermal effects occur at nearly identical temperatures. This suggests the formation of a mixed compound from the components of the Ba–Sr–Nb system coprecipitate, similar to that formed in the Ba–Nb system. It seems that the presence of barium in the system, even in low amount, favours the formation of the mixed compound. Another proof of mixed compound formation is provided by the infrared spectrum of the ternary system coprecipitate, which is

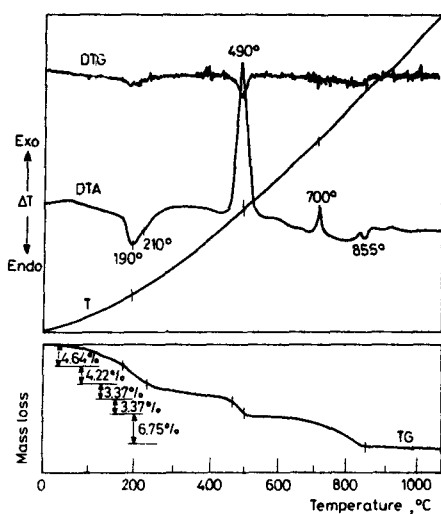


Fig. 7 TG and DTA curves of niobic acid – strontium oxalate – barium oxalate coprecipitate

Table 7 Thermal analysis data for niobic acid – strontium oxalate – barium oxalate coprecipitate

temperature, °C	Weight loss (TG)		Thermal effects, °C		Compounds
	% loss	lost species	endo	exo	
20–175	4.64	H ₂ O	190		Nb ₂ O ₅ · xH ₂ O + 0.29 BaC ₂ O ₄ · · 0.5 H ₂ O + 0.71 SrC ₂ O ₄ · H ₂ O
175–225	4.22		210		Nb ₂ O ₅ + (0.29 BaC ₂ O ₄ + + 0.71 SrC ₂ O ₄)
225–460	3.37				
460–500	3.37	CO, (1 - x)CO ₂		490	Nb ₂ O ₅ + (0.29 BaCO ₃ + + 0.71 SrCO ₃) · xCO ₂ ads.
500–860	6.75			700	Ba _{0.29} Sr _{0.71} Nb ₂ O ₆ · xCO ₂ ads.
860–1000	0.85	xCO ₂	855		Ba _{0.29} Sr _{0.71} Nb ₂ O ₆

nearly identical with that of the binary Ba–Nb coprecipitate, and differs markedly from those of simple barium and strontium oxalates (Table 8).

The dehydration of the coprecipitate is marked by two endothermic effects, at 190° and 210°, with elimination of 2.5 water molecules.

The decomposition of the mixed compound, with CO elimination, occurs gradually between 225° and 860°. The decarbonation is accompanied by an exothermic effect at 490°, identical with that found in the Ba–Nb system. The formation of the mixed

Table 8 Infrared spectra of the Ba–Sr–Nb system

BaC ₂ O ₄ · 0.5 H ₂ O cm ⁻¹	SrC ₂ O ₄ · H ₂ O cm ⁻¹	Coprecipitate cm ⁻¹	Ba _{0.29} Sr _{0.71} Nb ₂ O ₆ cm ⁻¹	Assignment
490 s	510 w	530 ww		δ(O–C=O)
660 m	600 w		600 w, br	ν(Nb–O)–niobate
725 w				
760 w	795 m	780 m		δ(O–C=O)
840 s	860 w, br			
1030 m				
1230 s				
1315 s	1320 s	1320 vs		ν(C–O), δ(O–C=O)
	1460 w	1430 w, br		ν(C–O), ν(C=C)
1640 s, br	1640 s	1625 vs		ν(C=O), (H ₂ O)
	1670 s			ν _{as} (C=O)

Table 9 X-ray diffraction lines of Ba_{0.29}Sr_{0.71}Nb₂O₆

<i>d</i> , Å	<i>hkl</i> ₀	<i>d</i> , Å	<i>hkl</i> ₀
4.4749	3	3.0593	100
3.9258	16	3.0214	27
3.8795	12	2.9291	9
3.6163	3	2.8821	5
3.4514	13	2.8456	10
3.3491	7	2.8086	12
3.2099	21	2.7783	41

Ba–Sr metaniobate is indicated by the endothermic effect at 700°. This temperature is identical with that of barium metaniobate formation.

It should be mentioned that the mixed barium–strontium metaniobate Ba_{0.29}Sr_{0.71}Nb₂O₆ has, so far, been obtained only by solid-phase reactions between niobium pentoxide and the corresponding carbonates, at temperature above 1200° and up to 1450° [13, 14], requiring prolonged thermal treatment.

The X-ray diffraction diagram of the thermal decomposition product (Table 9) confirms the formation of a mixed niobate Ba_{*x*}Sr_{1–*x*}Nb₂O₆ with tetragonal structure, of approximate composition Ba_{0.25}Sr_{0.75}Nb₂O₆ [15].

Experimental

A series of oxalatonioic acid and strontium nitrate solutions, of preestablished concentrations, were prepared in volumetric flasks.

The oxalatonioic acid solution was prepared by dissolving freshly precipitated niobic acid in an excess of oxalic acid (corresponding to a Nb:H₂C₂O₄ ratio of

1:5); the excess was necessary in order to ensure the stability of the solution on storage and to avoid precipitation of niobic acid. The concentrations of the stock solutions used in these experiments were as follows:

$$C_{\text{Nb-ox}} = 6.12 \cdot 10^{-2}M, \quad C_{\text{Ba(NO}_3)_2} = 3.06 \cdot 10^{-2}M$$

The concentrations were selected so as to have equal volumes on mixing Nb and Ba (or Sr + Ba) solutions, and to have a 2 Nb:1 Ba molar ratio.

A series of mixtures with constant Nb and Ba content (Nb:Ba = 2:1) were prepared in polyethylene flasks. To each flask, definite amounts of 2 N NH₄OH solution were added, according to the data shown on the potentiometric curve. The stoppered flasks were allowed to stand at room temperature for 2–3 h until equilibrium was established. The precipitates formed were filtered off and washed with water, and were then analyzed to establish the precipitation degree of Nb(V) and Ba(II). In the filtrates, the pH was determined immediately by potentiometric methods.

Niobium and barium were determined gravimetrically and the oxalate by permanganometric titration.

The precipitation degrees, i.e. the Nb(V) and Ba(II) percentages precipitated in each mixture, relative to the initial Nb(V) and Ba(II) contents, are shown in Figs 2 and 3.

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 Cu K_α radiation.

The TG and DTA curves were recorded with a Paulik–Paulik–Erdey MOM derivatograph, in air, with a heating rate of 5 deg/min.

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Zusammenfassung — Es wird eine neue, nicht-traditionelle Methode zur Synthese von Bariummetaniobat (BaNb_2O_6) und eines gemischten Barium—Strontium-Metaniobats ($\text{Ba}_{0,29}\text{Sr}_{0,71}\text{Nb}_2\text{O}_6$) durch thermische Zersetzung von Kopräzipitaten angegeben. Die Bedingungen der quantitativen Fällung der Metalle als Niobsäure und Bariumoxalat oder Barium—Strontium-Oxalat wurden ermittelt. Der Mechanismus der thermischen Zersetzung der Kopräzipitate wurde aus differentialthermoanalytischen und röntgendiffraktometrischen Daten abgeleitet. Bariummetaniobat bildet sich bei 740°C , also bei einer Temperatur, die unter der liegt, die bei der auf der Festkörperreaktion zwischen Nb_2O_5 und BaCO_3 basierenden Synthese aufzubringen ist (1100°C). Die gemischte Barium—Strontium-Verbindung wird bei einer Temperatur von 700°C gebildet, die niedriger als die für die Reaktion zwischen Nb_2O_5 , BaCO_3 und SrCO_3 notwendige Temperatur von 1100°C ist.

Резюме — Приводится новый метод синтеза метаниобата бария — BaNb_2O_6 и смешанного барий — стронций ниобата — $\text{Ba}_{0,29}\text{Sr}_{0,71}\text{Nb}_2\text{O}_6$, путем термического разложения соосажденных веществ. Определены условия количественного осаждения солей металлов ниобиевой кислоты и барий или же барий — стронций оксалатов. На основе данных ДТА и рентгено-дифракционного анализа установлен механизм термического разложения соосадков. Метаниобат бария образуется при 740°C , что значительно ниже температуры 1100°C , требуемой при твердотельной реакции между пятиокисью ниобия и карбонатом бария. Смешанный барий — стронций ниобат образуется при 700°C , что ниже температуры 1100°C , используемой в реакции между пятиокисью ниобия и карбонатами бария и стронция.