Thermochimica Acta, 102 (1986) 311–322
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

LANTHANOID TELLURITES

M. CELESTE S. PEREIRA and R.A. GUEDES DE CARVALHO
Centro de Engenharia Química, Faculdade de Engenharia, Porto (Portugal)
(Received 26 November 1985)

ABSTRACT

The preparation in aqueous medium of hydrogen and neutral tellurites of lanthanum, gadolinium and ytterbium is described.

Chemical analysis, solubilities in water, TG and DTA curves were determined and commented upon.

INTRODUCTION

The literature on the preparation and properties of lanthanoid sulphites [1–6] and selenites [7–11], as well as scandium selenites [12–17], is rather extensive.

Very few references were found, however, about lanthanoid tellurites. Compounds obtained by solid-state reaction were described by Redman et al. [18] and Weber et al. [19]. The only references found about preparation of lanthanoid tellurites in an aqueous medium were the works of Dobrowolski [20] and of Voloshina et al. [21], where some tellurites were obtained by the double decomposition of sodium tellurite and lanthanoid nitrates.

The preparation of tellurites (other than lanthanoids) in an aqueous medium is referred to by several authors. The methods used may be divided into two groups: double decomposition of solutions of metal salts (chloride or sulphate) and sodium (or potassium) tellurite [22–28] or dissolution of TeO_2 in hydroxide solutions [29–33]. The first method was used for Mg, Sr, Ba, Cu, Cd, Pb, Cr, Fe, Mn, Ni, Co and Zn tellurites, while the second method was used for Li, Na, K and Ba compounds.

Dobrowolski [20] describes the preparation by double decomposition of solutions of $Ln_2(NO_3)_3$ and Na_2TeO_3, using an excess of 10% of the tellurite necessary to give $Ln_2(TeO_3)_3$. Then, he says, "the liquid above the precipitate gave always an alkaline reaction and contained Na_2TeO_3". In these conditions the precipitates obtained always had the composition $Ln_2(TeO_3)_3$.

This same composition was determined by some physico-chemical methods by Voloshina and Oblonchik [21] in a recent work, when the preparation

0040-6031/86/$03.50

was made at $pH \geqslant 8.5$. However, as these authors say, these compounds, as well as the methods of preparation, are insufficiently studied.

The purpose of this work is to study carefully the preparation in an aqueous medium of some lanthanoid tellurites. Lanthanum, gadolinium and ytterbium were chosen, as representatives of the three groups of lanthanoids.

EXPERIMENTAL

Reagents and preparation of tellurites

All chemicals used were analytical grade, without further purification.

Tellurium dioxide behaves as an ampholyte with an isoelectric point, corresponding to the minimum solubility, occurring at pH 3.5–4.2 [34,35]. The lowest solubility observed [33] was 2.1 mg l^{-1} at pH 4.04. This very low solubility limits sharply the concentration of a H_2TeO_3 solution in the pH range of 3 to 6.

On the other hand the precipitation of lanthanoid hydroxides from an acid solution of its salts, begins when the pH reaches 6 to 8, depending on the lanthanoid and its concentration.

When the preparation of the lanthanoid tellurite is made by adding a solution of lanthanoid salt to a solution of tellurous acid, it is fundamental to define the concentration of the solutions and the final pH. Indeed if the final pH is on the acid side, it is possible that the precipitate will be a mixture of lanthanoid tellurite and H_2TeO_3. If the final pH is on the alkaline side it is possible that the precipitate will be lanthanoid tellurite contaminated with $Ln(OH)_3$ (basic tellurites) or the corresponding alkali tellurite (double tellurites).

It was decided to prepare an acid solution of TeO_2 (ca. 1.0 g dm^{-3}) in 1.0 M HCl and take aliquots from this which were adjusted, with NH_4OH, to pH 7.0, 8.0 and 9.0, respectively. Solubilities of TeO_2 at these pH were determined previously (Table 1).

Lanthanoid chloride solutions (ca. 0.005 M) in 10^{-3} M HCl, were adjusted, with diluted NH_4OH, up to pH 6.8.

TABLE 1

Solubility of TeO_2 in water with pH adjusted with NH_4OH

Initial pH	Solubility of TeO_2	
	($10^4 \times$ mol dm^{-3})	(mg dm^{-3})
7.0	0.98	15.6
8.0	1.67	26.6
9.0	2.35	37.5

Aliquots of lanthanoid and tellurium solutions corresponding to several ratios Te/Ln (1.5/1 to 6/1) were mixed, in every case adjusting the final pH of the mixture to the initial pH of the tellurium solution.

The flocculent precipitates formed were filtered the following day and washed with water adjusted to the same pH used in the preparation.

The precipitate was dried in a vacuum at 50°C until constant weight.

Chemical analysis

The chemical analysis of lanthanoid was performed by a spectrophotometric method with arsenazo III [36], and total Te by reduction to elemental tellurium with SO_2 + hydrazine [37].

After solubilization of the salt with diluted HCl (1:10) tellurium was separated by the described method [37].

Lanthanoid was determined in the filtrate by arsenazo III method [36], after destroying hydrazine by evaporating to a small volume, adding concentrated $H_2SO_4 + HNO_3$ (5 ml + 2 ml), evaporating to dryness, heating until no more white fumes of SO_3 were evolved, diluting with small amount of HCl, evaporating to dryness again and diluting with 3 M HCl.

An analysis of Te(IV) was done by the method described by Bart et al. [38].

Solubility

Stoppered glass tubes of 60 ml, containing 50 ml of water and 0.2 g of tellurite, were fixed to a rotating wheel and immersed in a thermostatic water bath at 25°C, for 7 days.

Aliquots of the filtered solution were taken for determinations of Te [37] and Ln [36].

Thermogravimetry and X-ray diffraction

Thermograms were obtained with a Mettler Thermoanalyzer 2.

X-ray diffraction patterns were obtained on a Philips diffractometer using Cu K_α radiation.

RESULTS AND DISCUSSION

Preparation of tellurites

According to the results shown in Table 2 the salts obtained at pH = 7.0, after being dried in a vacuum at 50°C, are hydrogen tellurites with the general formula $Ln(HTeO_3)_3$.

TABLE 2

Chemical analysis of La, Gd and Yb tellurites prepared at pH = 7.0 and dried at 50°C under vacuum

Elements	$La(HTeO_3)_3$		$Gd(HTeO_3)_3$		$Yb(HTeO_3)_3$	
	Theor. (%)	Exp. (%)	Theor. (%)	Exp. (%)	Theor. (%)	Exp. (%)
Tellurium	57.06	57.50	55.54	55.34	54.30	54.40
Lanthanoid	20.77	20.79	22.89	22.88	24.61	24.63

Salts prepared at pH = 9.0, dried in the same way, are neutral tellurites with the general formula $Ln_2(TeO_3)_3 \cdot xH_2O$, as shown in Table 3.

At pH = 8.0, a lanthanum hydrogen tellurite was prepared with a composition approximately $LnH(TeO_3)_2$ (or $Ln_2(TeO_3)_3 \cdot H_2TeO_3$).

The only lanthanoid tellurites prepared in an aqueous medium [20,21] were obtained in alkaline medium (alkalinity not specified) and had the general formula $Ln_2(TeO_3)_3 \cdot xH_2O$ ($x = 4$ to 6).

Hydrogen tellurites had yet to be referred to in the literature either for lanthanoids or other elements, because most of the authors [20–33] worked in alkaline media, where TeO_3^{2-} species predominate.

Nabivanets et al. [39] presents a diagram illustrating the state of Te(IV) in perchlorate solutions, where it can be seen that between pH 4 and 7 the species $HTeO_3^-$ is predominant to about 100%, at pH 8 the ratio of species $HTeO_3^- : TeO_3^{2-} = 1:1$, and at pH 9 the same ratio is 1 : 9. The composition of the tellurites presented in this work (Tables 2 and 3) confirms the diagram of Nabivanets.

In the preparation of tellurites at pH 9 the molar ratio Te : Ln must be higher than the theoretical 3 : 2, in order to prevent the possible formation of basic tellurites of the general formula $xLn_2(TeO_3)_3 \cdot yLn(OH)_3$, which were described for Cu, Ni and Co salts [23,25] when preparation was made at high pH values.

The literature on rare earth selenites show that salts obtained with Se(IV) are similar to those described in the present work with Te(IV). Giesbrecht et

TABLE 3

Chemical analysis of La, Gd and Yb tellurites prepared at pH = 9.0 and dried at 50°C under vacuum

Elements	$La_2(TeO_3)_3 \cdot 6H_2O$		$Gd_2(TeO_3)_3 \cdot 6H_2O$		$Yb_2(TeO_3)_3 \cdot 5H_2O$	
	Theor. (%)	Exp. (%)	Theor. (%)	Exp. (%)	Theor. (%)	Exp. (%)
Tellurium	52.47	52.61	50.44	50.62	49.72	50.02
Lanthanoid	35.70	35.63	38.19	38.31	40.93	40.98

TABLE 4

Solubility in water at 25°C of $Ln(HTeO_3)_3$ and $Ln_2(TeO_3)_3 \cdot xH_2O$

Ln	$Ln(HTeO_3)_3$	$Ln_2(TeO_3)_3 \cdot xH_2O$
	Solubility ($\times 10^3$) (g dm^{-3})	Solubility ($\times 10^4$) (g dm^{-3})
La	12.5	36.9
Gd	21.8	41.5
Yb	12.2	51.5

al. [9] prepared $Ln_2(SeO_3)_3 \cdot nH_2O$ ($n = 4$ to 5) by mixing stoichiometric quantities of $LnCl_3$ and Na_2TeO_3 solutions, while Immonen et al. [11] and Giesbrecht et al. [8] obtained hydrogen selenites ($LnH(SeO_3)_2 \cdot 2.5H_2O$) when using an excess of selenious acid in the preparation.

Znamenskaya et al. [12–15,17] refer to the preparation in an aqueous medium of scandium selenites $Sc_2O(SeO_3)_2 \cdot 3H_2O$ and $Sc_2(SeO_3)_3 \cdot 5H_2O$ obtained in alkaline media, and $ScH(SeO_3)_2 \cdot H_2O$ and $Sc(HSeO_3)_3$ obtained in acidic media.

Solubilities

The solubility in water (see Table 4) of the prepared tellurites was determined by the method described earlier [40].

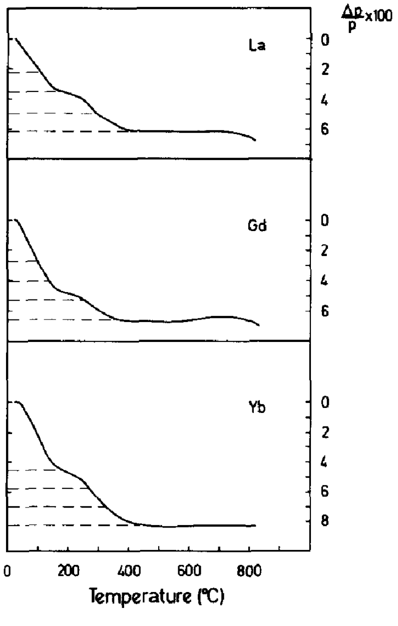

Fig. 1. TGA curves of hydrogen tellurites—$Ln(HTeO_3)_3$.

Thermal analysis

TGA curves of hydrogen tellurites ($Ln(HTeO_3)_3$)

The loss of weight up to 400–500°C observed in the thermograms of Fig. 1 may be assigned to hygroscopic water (ca. 2 moles in the case of La and Gd salts, and 3 moles in the Yb salt) and to decomposition of the dry salt according to

$$2Ln(HTeO_3)_3 \rightarrow Ln_2O_3 \cdot 6TeO_2 + 3H_2O$$

It was observed that these salts are very hygroscopic which justifies the high levels of humidity absorbed during the weighing of the samples and initial stabilization of the thermoanalyzer.

The slope of TG curves may be interpreted by the following scheme

$$2La(HTeO_3)_3 \xrightarrow[-1H_2O]{100-200^\circ C} La_2(TeO_3)_3 \cdot 3TeO_2 \cdot 2H_2O$$

$$\xrightarrow[-2H_2O]{200-450^\circ C} La_2(TeO_3)_3 \cdot 3TeO_2$$

$$2Gd(HTeO_3)_3 \xrightarrow[-1.5H_2O]{100-200^\circ C} Gd_2(TeO_3)_3 \cdot 3TeO_2 \cdot 1.5H_2O$$

$$\xrightarrow[-1.5H_2O]{200-400^\circ C} Gd_2(TeO_3)_3 \cdot 3TeO_2$$

$$2Yb(HTeO_3)_3 \xrightarrow[-3H_2O]{200-400^\circ C} Yb_2(TeO_3)_3 \cdot 3TeO_2$$

Between 450–600°C there is a well-defined plateau where the elemental composition is given in Table 5.

In the case of the Gd salt an increase in weight of about 0.3% was noticed between 550 and 780°C, while La and Yb salts exhibit only a slight tendency to weight increase, which may be explained by partial oxidation of Te(IV) to Te(VI).

Indeed Sokolov et al. [27], Frit and Hagenmuller [41] and Frit and Jaymes [42] observed that on heating Cr, Al or In tellurites between 570 and 720°C,

TABLE 5

Chemical analysis [a] of La, Gd and Yb hydrogen tellurites after heating at 600°C for 2 h

Elements	$La_2(TeO_3)_3 \cdot 3TeO_2$		$Gd_2(TeO_3)_3 \cdot 3TeO_2$		$Yb_2(TeO_3)_3 \cdot 3TeO_2$	
	Theor. (%)	Exp. (%)	Theor. (%)	Exp. (%)	Theor. (%)	Exp. (%)
Tellurium	59.65	59.66	58.00	57.86	56.64	56.56
Lanthanoid	21.65	21.35	23.82	23.56	25.60	25.61

[a] The analysis showed that all the tellurium is Te(IV).

an increase in the weight occurred, which was interpreted as an oxidation of one third of the tellurium present according to the reaction

$2Cr_2Te_3O_4 + O_2 \rightarrow Cr_2TeO_6 + 4TeO_2$

If the mechanism proposed is applied to Gd tellurite

$2Gd_2O_3 \cdot 6TeO_2 + O_2 \rightarrow 2Gd_2O_3 \cdot TeO_3 + 10TeO_2$

an increase of 1.2% in weight should be observed.

As the observed increase was only 0.3% this means that the proposed reaction is only partly accomplished, or the loss of TeO_2 observed in that range of temperature compensates for the increase that should be observed.

Above 700°C a loss of weight was observed in all TGA curves which was due probably to the volatilization of TeO_2. In order to confirm this assumption a sample of 100 mg of $Yb(HTeO_3)_3$ was heated for 40 min at 1000°C and analysed for Yb, Te(IV) and Te (total). No loss of Yb occurred, 17% of total Te was lost and 23% of the remaining Te was oxidized to Te(VI).

Voloshina et al. [43] studied lanthanide tellurites by IR spectroscopy but they did not detect (in samples heated up to 700°C) the characteristic peaks of the TeO_6^{6-} ion, concluding that there is no oxidation of Te(IV) to Te(VI) on heating.

TGA curves of neutral tellurites ($Ln_2(TeO_3)_3$)

The loss of weight up to 500°C observed in TGA curves (Fig. 2) of the

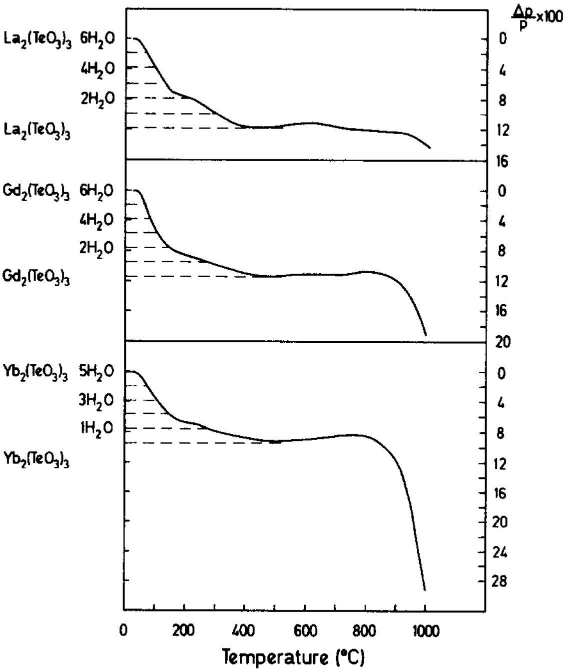

Fig. 2. TGA curves of neutral tellurites—$Ln_2(TeO_3)_3 \cdot xH_2O$.

TABLE 6

Chemical analyses [a] of La, Gd and Yb tellurites after heating up to 500°C and left to cool in the thermobalance

Elements	La			Gd			Yb		
	Exp.	Theoretical		Exp.	Theoretical		Exp.	Theoretical	
		$La_2Te_3O_9$	$La_2Te_3O_{12}$		$Gd_2Te_3O_9$	$Gd_2Te_3O_{12}$		$Yb_2Te_3O_9$	$Yb_2Te_3O_{12}$
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Tellurium	45.14	47.58	44.90	43.80	45.50	43.05	41.96	43.86	41.57
Lanthanoid	32.76	34.53	32.58	35.02	37.38	35.36	37.89	39.65	37.58

[a] The analyses showed that 2 to 4% of the tellurium is Te(VI).

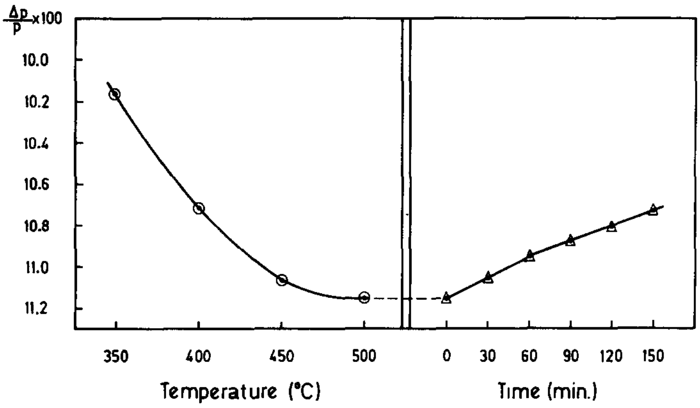

Fig. 3. Partial TGA curve of $Gd_2(TeO_3)_3 \cdot 6H_2O$ up to 500°C ($\Delta T = 2°C\ min^{-1}$) followed by 150 min of isothermal heating at 500°C.

three tellurites studied, may be assigned to the loss of 6 water molecules of La and Gd salts, and of 5 water molecules of the Yb tellurite.

From the shape of the curves it seems that the last molecules of water are more strongly bound than the others. In fact at 200°C it may be observed that La tellurite still retains 2 molecules of water and Gd and Yb salts retain 1.5 molecules.

At 500°C all the tellurites are anhydrous, but between 500°C and 800°C slight increases of weight are observed which may be explained by the mechanism described for TGA of hydrogen tellurite of Gd, i.e., by a partial fixation of oxygen.

In Table 6 the compositions of the tellurites heated up to 500°C and left to cool in the thermobalance are given.

According to the figures and the detection of Te(VI) in the samples, the slight increase in weight may be explained by the partial oxidation of Te(IV) to Te(VI).

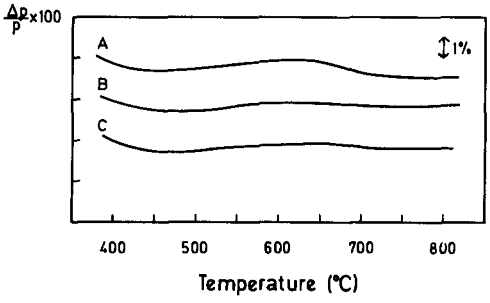

Fig. 4. Partial TGA curves of $La_2(TeO_3)_3 \cdot 6H_2O$ using different atmospheres: (A) air; (B) nitrogen (> 99.5%); (C) pure nitrogen (≫ 99.7%).

Products obtained at 500°C are unstable at that temperature as shown by the experiment represented in Fig. 3, where a sample of $Gd_2(TeO_3)_3 \cdot 6H_2O$ was heated up to 500°C ($\Delta T = 2°C\ min^{-1}$) and then maintained isothermally at that temperature for 150 min. An increase in weight of about 0.4% was observed and the analysis of the product showed that 13% of the total tellurium was present as Te(VI).

Another evidence for the presence of oxygen being fundamental for the increase of weight is given in Fig. 4, where it can be seen that the weight increase depends on the oxygen content of the gas used in the TGA.

Above 800°C the steep slope of TGA curves indicates loss of tellurium as TeO_2.

DTA curves of hydrogen and neutral tellurites

Figure 5 shows the DTA curves of hydrogen tellurites of lanthanum and ytterbium.

The first endothermic peak with a minimum at about 100°C is probably due to the loss of hygroscopic water.

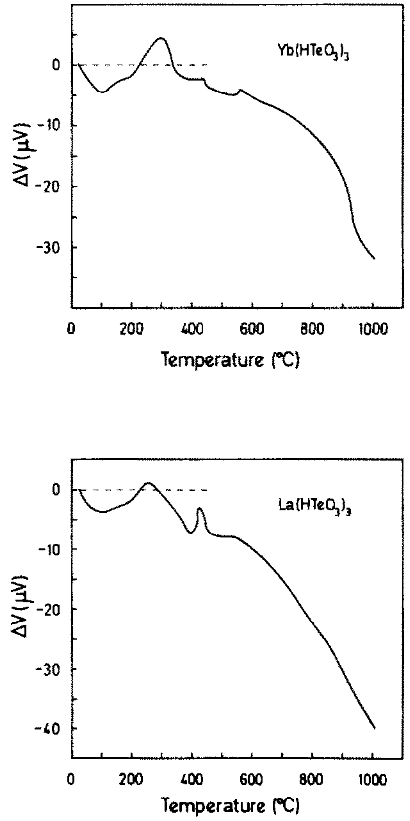

Fig. 5. DTA curves of $Yb(HTeO_3)_3$ and $La(HTeO_3)_3$; heating rate = $2°C\ min^{-1}$.

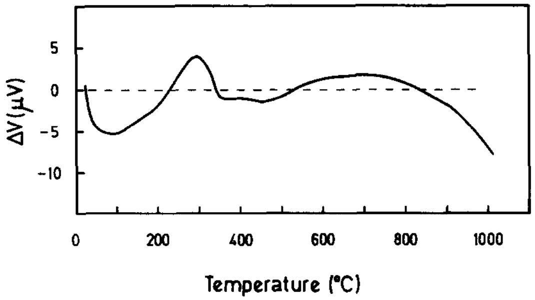

Fig. 6. DTA curve of $La_2(TeO_3)_3 \cdot 6H_2O$; heating rate = 2°C min^{-1}.

The exothermic peak at about 250–300°C is probably due to the rearrangement of the molecules and is immediately followed by an endothermic peak resulting from the loss of molecules of water.

At 400–450°C a slight exothermic peak can be seen that could be assigned to a rearrangement of the structure of the molecules; according to Bart et al. [38] this is a possibility.

The slight exothermic peak at 500°C in the Yb salt could be justified by a slight fixation of oxygen which was observed in the TGA curves.

Above 600°C a sharp endothermic peak resulting from the loss of TeO_2 was observed.

Figure 6 shows the DTA curve of the neutral tellurite of lanthanum.

It seems that the loss of the first 3 molecules of water is endothermic and the rearrangement of the molecule and loss of the last 3 water molecules is exothermic.

From about 500 to 800°C a slight exothermic peak can be seen which may be assigned to the apparent fixation of oxygen with partial oxidation of Te(IV) to Te(VI).

X-ray diffraction

Hydrogen tellurites of La, Gd and Yb were observed by X-ray diffraction immediately after the preparation and after 1 month. In all the cases the salts were amorphous.

After heating at 600°C all gave crystalline patterns.

REFERENCES

1 R.C. Vickery, J. Chem. Soc., (1955) 2360.
2 C. Castellani Bisi and M. Cola, Gazz. Chim. Ital., 92 (1962) 447.
3 C. Castellani Bisi and A. Clerici, Gazz. Chim. Ital., 93 (1963) 1444.
4 A.A. Grizik and N. Abdulina, Russ. J. Inorg. Chem. (English Transl.), 16 (1971) 965.
5 L. Niinistö and M. Koskenlinna, Suom. Kemistil., B46 (1973) 245.
6 V.I. Moskalenko, L.G. Korotaeva, A.K. Molodkin and N. Pen'ya, Russ. J. Inorg. Chem. (English Transl.), 21 (1976) 957.

7 R.L. Espil, Compt. Rend., 152 (1911) 378.

8 E. Giesbrecht, G. Vicentini and L. Barbieri, An. Acad. Brasil. Cienc., 40 (1968) 453.

9 E. Giesbrecht, M. Perrier and W.W. Wendlandt, An. Acad. Brasil. Cienc., 34 (1962) 37; E Giesbrecht and I. Giolito, An. Acad. Brasil. Cienc., 39 (1967) 233.

10 O. Erämetsä, T. Pakkanen and L. Niinistö, Suom. Kemistil., B46 (1973) 330.

11 E. Immonen, M. Koskenlinna, L. Niinistö and T. Pakkanen, Finnish Chem. Lett., (1976) 67.

12 A.S. Znamenskaya, L.N. Komissarova and V.I. Spitsyn, Russ. J. Inorg. Chem. (English Transl.), 17 (1972) 947.

13 A.S. Znamenskaya and L.N. Komissarova, Russ. J. Inorg. Chem. (English Transl.), 18 (1973) 458.

14 L.N. Komissarova and A.S. Znamenskaya, Russ. J. Inorg. Chem. (English Transl.), 19 (1974) 159.

15 A.S. Znamenskaya, L.N. Komissarova and V.M. Shatskii, Russ. J. Inorg. Chem. (English Transl.), 22 (1977) 1150; 22 (1977) 1654.

16 J. Valkonen and M. Leskelä, Acta Crystallogr., Sect. B, 34 (1978) 1323.

17 A.S. Znamenskaya, L.N. Komissarova and K.I. Petrov, Koord. Khim., 5 (8) (1979) 1180.

18 M.J. Redman, W.P. Binnie and J.R. Carter, J. Less-Common Met., 16 (1968) 407.

19 M.J. Weber, J.D. Myers and D.H. Blackburn, J. Appl. Phys., 52 (1981) 2944.

20 I. Dobrovolsky, Rockzniki Chem., 40 (1966) 1169.

21 A.L. Voloshina and V.A. Oblonchik, Ukr. Khim. Zh., 48 (10) (1982) 1028.

22 V. Lenher and E. Wolesensky, J. Am. Chem. Soc., 35 (1913) 718.

23 V.S. Yakovleva and E. Sh. Ganelina, Russ. J. Inorg. Chem. (English Transl.), 4 (1959) 233.

24 G. Gattow and O.J. Lieder, Naturwissenschaften, 50 (1963) 662.

25 E. Sh. Ganelina, Zh. Prikl. Kh., 40 (1967) 1019.

26 E.A. Ivankova, K.K. Samplavskaya and M. Kh. Karapet'yants, Izv. Akad. Nauk SSSR, Neorg. Mater, 3 (1967) 1712.

27 Yu. N. Sokolov, K.K. Samplavskaya and M.Kh. Karapet'yants, Russ. J. Phys. Chem. (English Transl.), 49 (1975) 1603.

28 Yu. N. Sokolov, K.K. Samplavskaya and M. Kh. Karapet'yants, Russ. J. Inorg. Chem. (English Transl.), 21 (1976) 344.

29 O.I. Vorob'eva and E.A. Lavut, Russ. J. Inorg. Chem. (English Transl.), 3 (1958) 20.

30 O.N. Brensov, T.V. Revzina and N.A. Druz, Russ. J. Inorg. Chem. (English Transl.), 10 (1965) 1084.

31 B.R. Nielsen, R.G. Hazell and S.E. Rasmussen, Acta Chem. Scand., 25 (1971) 3037.

32 E. Philippot, M. Maurin and J. Moret, Acta Crystallogr., Sect. B, 35 (1979) 1337.

33 F. Daniel, J. Moret, M. Maurin and E. Philippot, Acta Crystallogr., Sect. B, 38 (1982) 703.

34 I.M. Issa and S.A. Awad, J. Phys. Chem., 58 (1954) 948.

35 M. Haïsinsky and M. Cottin, Anal. Chim. Acta, 3 (1949) 226.

36 S.B. Savvin and A.A. Muk, Bull. Inst. Nucl. Sci., 12 (1961) 97.

37 W.R. Schoeller and A.R. Powell, The Analysis of Minerals and Ores of the Rarer Elements, 3rd edn., Charles Griffin, London, 1955.

38 J.C.J. Bart, A. Rossi, R. Perissinoto, A. Castellan and N. Giordano, J. Therm. Anal., 8 (1975) 313.

39 B.I. Nabivanets, E.E. Kapantsyan and E.N. Oganesyan, Russ. J. Inorg. Chem. (English Transl.), 19 (1974) 394.

40 C.G. González and R.A. Guedes de Carvalho, Thermochim. Acta, 24 (1978) 167.

41 B. Frit and P. Hagenmuller, Bull. Soc. Chim. Fr., 7 (1970) 2491.

42 B. Frit and M. Jaymes, Bull. Soc. Chim. Fr., 3-4 (1974) 402.

43 A.L. Voloshina, L.A. Ivantchenko, V.A. Obolontchik and V.A. Serdyuk, Ukr. Khim. Zh., 50 (1984) 383.