LANTHANOID AND YTTRIUM TELLURATES

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ABSTRACT

Preparation in aqueous medium of all the lanthanoid (except Ce and Pm) and yttrium tellurates is described. Chemical analyses, solubilities at 25°C in water and thermograms of all the products prepared were determined. X-ray diffractograms and DTA and DTG curves of La, Gd and Yb tellurates were obtained and commented. Partial volatilization of lanthanoid is observed in the thermal analysis of tellurates.

INTRODUCTION

The literature on the preparation and properties of lanthanoid sulphates[1−6] and selenates[7−9] is rather extensive.

However, very few references are found about lanthanoid tellurates. Natansohn[10] describes the synthesis of 14 rare-earth tellurates (Ln_2TeO_6) by reacting equimolar quantities of rare-earth sesquioxides, R_2O_3, and orthotelluric acid, $Te(OH)_6$, at elevated temperatures (800–1000°C). Blasse[11] prepares 6 rare-earth tellurates (Ln_6TeO_{12}) by heating a mixture of Ln_2O_3 and TeO_2 in oxygen, first at 900°C and then at 1100°C.

The only reference found about the preparation of lanthanoid tellurates in aqueous medium is the work of Montignie[12], where $Ce_2(TeO_4)_3$ is obtained by double decomposition of sodium tellurate and cerous nitrate.

This work presents data on the preparation in aqueous medium of all the lanthanoid (except Ce and Pm) and yttrium tellurates having the formula $Ln_2(TeO_4)_3$, which have not been described in the literature to date.

EXPERIMENTAL

Reagents

All the chemicals used were analytical grade, without further purification.

Preparation of tellurates

Double decomposition of solutions of K_2TeO_4 and $LnCl_3$ (3:2), at pH < 4, was unsuccessful.

TABLE I

CHEMICAL ANALYSIS OF La, Gd AND Yb TELLURATES

Elements	$La_2(TeO_4)_3$		$Gd_2(TeO_4)_3$		$Yb_2(TeO_4)_3$	
	Theor. (%)	Exp. (%)	Theor. (%)	Exp. (%)	Theor. (%)	Exp. (%)
Tellurium	44.9	45.1	43.1	42.7	41.6	41.0
Lanthanoid	32.6	32.9	35.4	35.0	37.6	37.9

Other tentatives, also unsuccessful, were made by the reaction of an aqueous suspension of $Ln_2(CO_3)_3$ freshly prepared with a solution of telluric acid (La:Te = 2:3).

The method that succeeded was the addition of NH_4OH to a solution of $LnCl_3$ and $Te(OH)_6$ (Ln:Te = 2:3 or 2:6) up to pH = 4.5 when a flocculent precipitate was observed.

This precipitate was filtered, washed and dried in vacuo at 50°C. Chemical analysis of lanthanoid (oxalate precipitation[13]) and tellurium (reduction to elemental tellurium with SO_2 + hydrazine[14]), performed on the salts of La, Gd and Yb, gave the results indicated in Table I.

Analysis of water (Karl Fisher method) and ammonium (Nessler method) in these salts, revealed only traces, showing that the drying was complete and the absence of possible double salts of Ln and NH_4.

Solubility

Stoppered glass tubes containing 50 ml of water and 0.2 g of salt 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 determination of tellurium[14] and lanthanoid (arsenazo III method[15]).

Thermogravimetry

Thermograms were obtained with a Mettler Thermoanalyzer 2.

X-ray diffraction

X-ray diffraction patterns were obtained on a Philips PW diffractometer using CuK_α radiation.

RESULTS AND DISCUSSION

Synthesis of all the lanthanoid (with exception of Ce and Pm) and yttrium tellurates, was accomplished under the conditions described.

Typical analyses of tellurates of La, Gd and Yb, given in Table 1, are consistent with the general formulation $Ln_2(TeO_4)_3$.

TABLE 2

SOLUBILITIES IN WATER, AT 25.0°C, OF YTTRIUM AND LANTHANOID TELLURATES (Ln$_2$(TeO$_6$)$_3$)

Ln	Solubility ($\times 10^6$) ($g\, l^{-1}$)	Ln	Solubility ($\times 10^6$) ($g\, l^{-1}$)
Y	60	Tb	20
La	20	Dy	36
Pr	28	Ho	42
Nd	64	Er	274
Sm	6	Tm	78
Eu	64	Yb	20
Gd	58	Lu	184

Ammonium hydroxide was preferred to sodium or potassium hydroxides to increase the pH of the solution in the preparation of tellurates because, due to the low solubility of Na and K tellurates, co-precipitation of these salts or formation of double tellurate was possible. As referred formerly, contamination with NH_4^+ was not observed.

Increasing the pH above 4.5 would certainly improve the yield of the synthesis, but there was the possibility of competition between OH^- and TeO_4^{2-}, with formation of hydroxo-tellurates.

In a recent paper[16], where Al, Ga and In tellurates are prepared by a method similar to that used in the present work, it is noticed that it is impossible to prepare tellurates by the interaction of freshly precipitated Ga hydroxide with telluric acid (at 25 and 100°C).

All the tellurates are rather insoluble in water, as shown in Table 2.

These very low solubilities suggest the possibility of using tellurate as a quantitative precipitating agent of lanthanoids.

Thermograms of all the tellurates (Fig. 1) exhibit a similar shape, with two well-defined plateaus at 300–450°C and 700–850°C. A third plateau, not well defined in some thermograms, is observed in the range 520–600°C.

Above 800–850°C a net loss of weight is noticed up to 1000°C, the maximum temperature obtainable in our thermoanalyser.

In order to understand the mechanism of the thermal decomposition, three tellurates were used to take samples for analysis after heating up to 400, 750 and 1000°C. Tellurates of La, Gd and Yb were chosen, as representatives of the three groups of lanthanoids. Their thermograms and points where the samples were taken are represented in Fig. 2.

Lanthanoid and tellurium contents of those samples are given in Table 3. Corresponding formal compositions are given in Table 4.

As may be observed in Fig. 2, the composition of the samples taken does not correspond to the plateaus where they were taken. In most cases, it was observed that loss of weight is much higher than revealed by chemical analysis. Obviously,
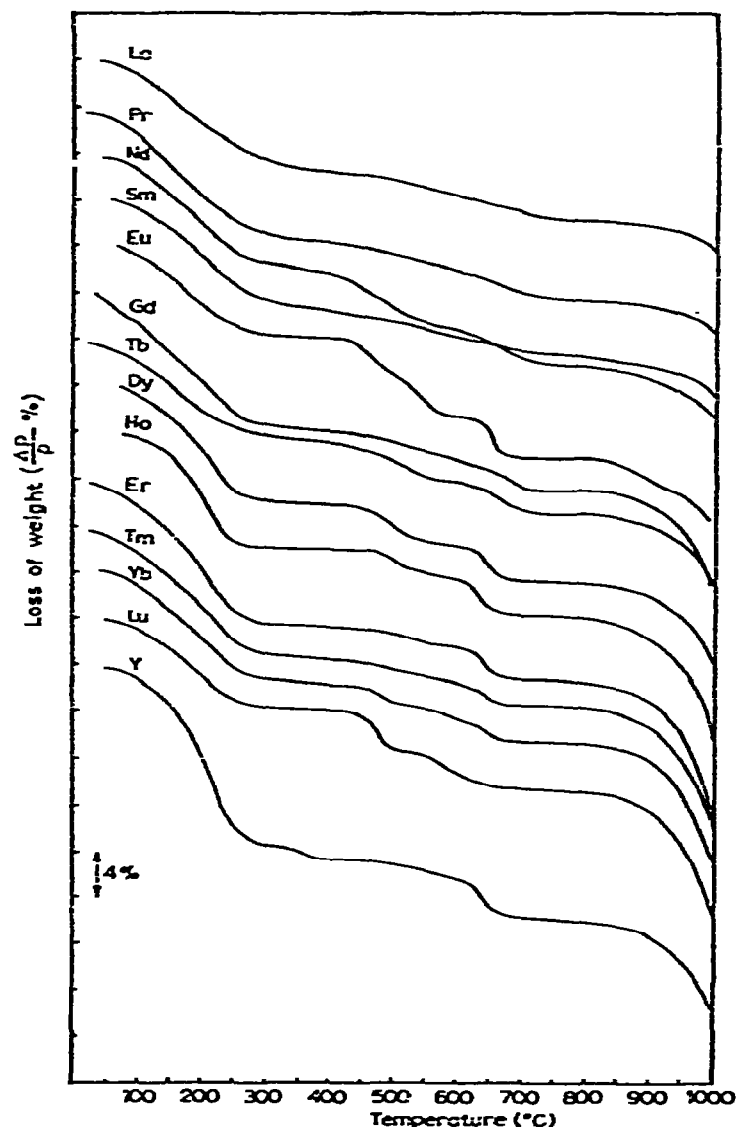
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Fig. 1. Thermograms of lanthanoid (except Ce and Pm) and yttrium tellurates $(Ln_2(TeO_4)_3)$.

this means that the lanthanoid is partially volatilized. In order to check this assumption, gaseous products obtained from the heating of samples were condensed and analysed. Tellurium and lanthanoid were found in this condensate.

Analyses performed using the total amount of sample used, confirmed loss of lanthanoid as well as tellurium by volatilization. The loss of each element, expressed as percent of initial content, is given in Table 5. The loss of oxygen on heating bismuth tellurate[17] and telluric acid[18], with consequent partial reduction of Te (VI) to Te (IV), has been noticed. In the present case, an experimental confirmation of this partial reduction was made, analysing total Te and Te(IV)[18] present in a sample
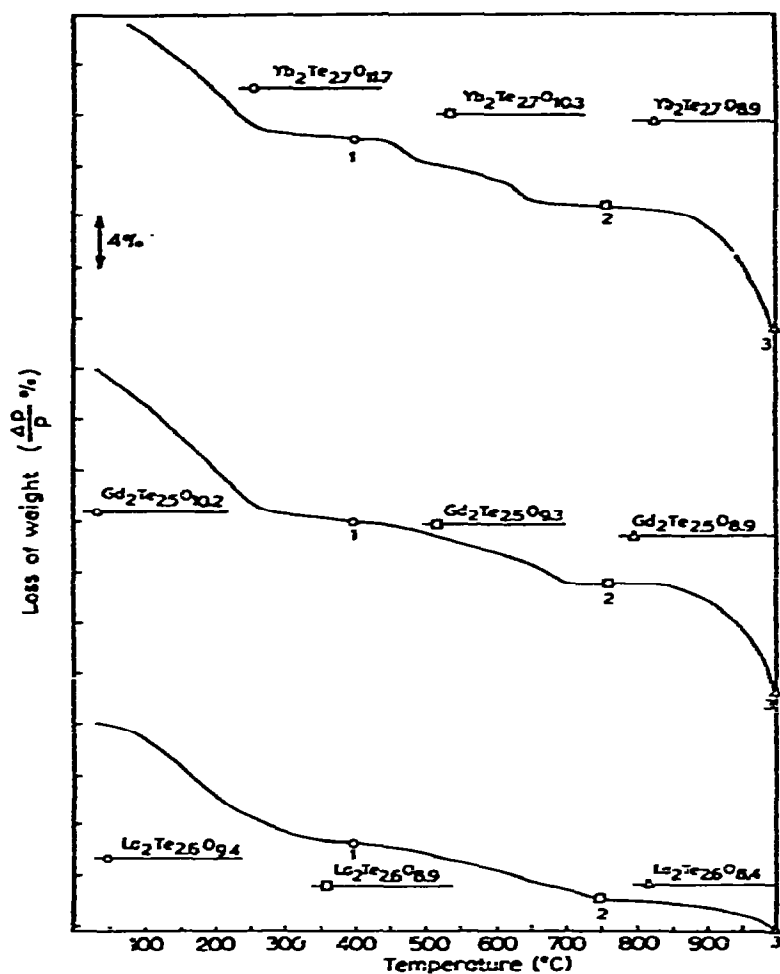
Fig. 2. Thermograms of Yb, Gd and La tellurates with indication of points (1, 2, 3) where samples were taken. Composition of each point is indicated above a straight line that corresponds to the loss of weight that should be observed if there was no volatilization of lanthanoid.

TABLE 3

ANALYSIS OF INTERMEDIATE PRODUCTS OBTAINED BY THERMAL DECOMPOSITION OF La, Gd AND Yb TELLURATES

Product	La (%)	Te (%)	Gd (%)	Te (%)	Yb (%)	Te (%)
$Ln_2(TeO_4)_3$	32.6	44.9	35.4	43.1	37.6	41.6
Heated up to 400°C	36.3	43.5	39.7	39.7	39.5	38.1
Heated up to 750°C	36.9	44.3	40.2	40.8	40.7	39.9
Heated up to 1000°C	37.1	44.9	40.7	40.7	41.0	40.5

TABLE 4

FORMAL COMPOSITION OF THE PRODUCTS OF TABLE 3

Product	Lanthanum	Gadolinium	Ytterbium
$Ln_2(TeO_4)_3$	$La_2Te_3O_{12}$	$Gd_2Te_3O_{12}$	$Yb_2Te_3O_{12}$
Heated up to 400°C	$La_2Te_{2.6}O_{9.6}$	$Gd_2Te_{2.5}O_{10.2}$	$Yb_2Te_{2.7}O_{11.7}$
Heated up to 750°C	$La_2Te_{2.6}O_{8.9}$	$Gd_2Te_{2.5}O_{9.3}$	$Yb_2Te_{2.7}O_{10.3}$
Heated up to 1000°C	$La_2Te_{2.6}O_{8.4}$	$Gd_2Te_{2.5}O_{8.9}$	$Yb_2Te_{2.7}O_{9.6}$

of $La_2(TeO_4)_3$ heated at 1000°C. It was found that about 70% of tellurium present was Te(IV).

However, the volatilization of lanthanoid is a very interesting fact not yet noticed by other authors. It seems that up to the first plateau (ca. 400–450°C), there is loss of oxygen, tellurium and small amounts of the heavier lanthanoids (Gd and Yb). Above this temperature and up to 1000°C, it is curious to notice that the ratio Ln:Te of the residual product remains constant with a value of about 2:2.6. This means that this same ratio should be observed in the volatile products.

As may be observed the volatilization of the lanthanoid increases with the increase of atomic number. We have no explanation for this anomalous observation.
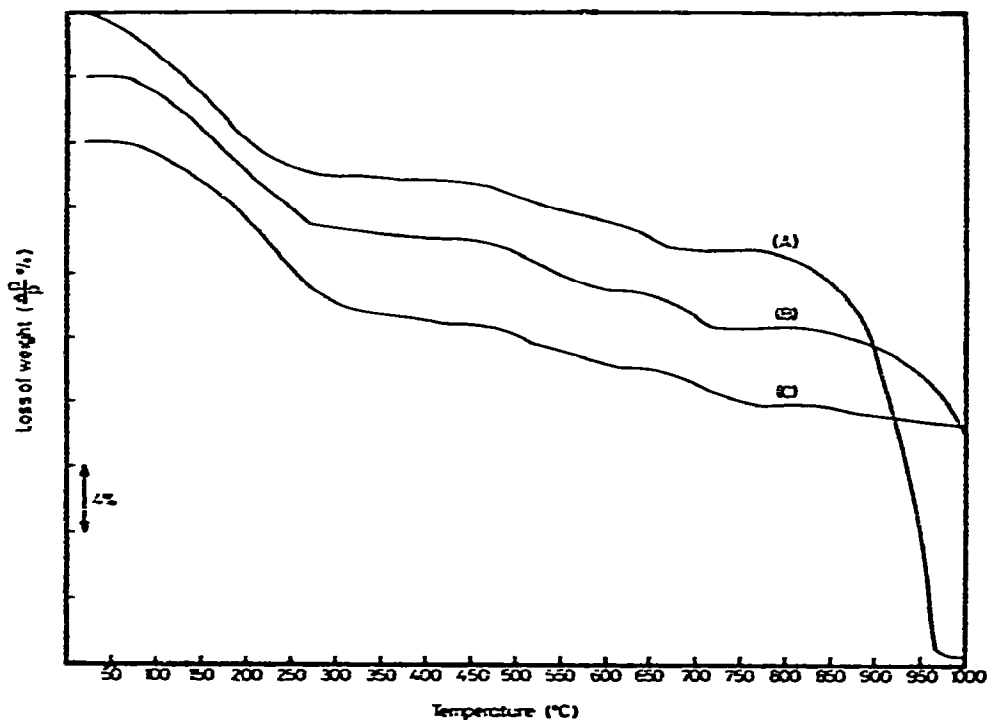

Fig. 3. Thermograms of $Gd_2(TeO_4)_3$ at three heating rates: (A), at 0.5°C min⁻¹; (B), at 4°Cm in⁻¹; (C), at 25°C min⁻¹.

TABLE 5

LOSS OF LANTHANOID, TELLURIUM AND OXYGEN AT EACH POINT INDICATED IN FIG. 2 (as percent of initial element present)

Initital compound	Loss of element(Δ)	Loss of weight (%)		
		Point 1 (400°C)	Point 2 (750°C)	Point 3 (1000°C)
La₂(TeO₄)₃	ΔLa	0	2.4	4.8
	ΔTe	12.3	15.0	16.3
	ΔO	18.8	28.1	33.1
Gd₂(TeO₄)₃	ΔGd	1.2	5.7	13.8
	ΔTe	18.9	21.4	29.1
	ΔO	15.8	26.4	34.9
Yb₂(TeO₄)₃	ΔYb	5.4	8.2	18.8
	ΔTe	17.5	18.6	27.5
	ΔO	2.8	20.8	33.6

There is no notice in the literature of volatile oxygenated salts of lanthanoids. The extensive work of Flahaut[19] about sulphides, selenides and tellurides of rare-earths and the corresponding oxy-salts, does not mention any volatile compounds of this type. The only reference found[20] is about partial vaporization of La_2S_3, at 1300–1400°C. Selenides and tellurides should vaporize at lower temperatures than sulphides, but, without further experimental evidence, it is daring to try to explain the vaporization by reduction of tellurate to tellurite and finally to a volatile telluride.

If the hypothesis of the formation of a telluride is admitted, the higher volatilization of the heavier lanthanoids could be explained by the decrease from 9 to 6 in coordination number of lanthanoids in tellurides through the series[19]. On the other hand. as the valence +2 of lanthanoids is favoured in their chalcogenides when going from sulphides to tellurides, the probable formation of $YbTe$[19] could be another reason for the higher volatilization of this element.

The fact that the six-valent S and Se oxy-acids are four-coordinated, while those of Te are six-coordinated, may explain the quite different thermogravimetric behaviour of selenates[9] and sulphates[3] when compared with that of tellurates described in this paper.

The influence of heating rate may be observed in Fig. 3. Although the general shape is maintained, it is observed that the loss of weight is favoured, either in the first zone (up to 200°C) or in the last one (800–1000°C) by a slow heating rate.

This fact may be explained if an isothermal loss of oxygen is observed as it is cited by Bart et al.[18] in thermal decomposition of telluric acid.

Figure 4 represents DTG and DTA curves for $Gd_2(TeO_4)_3$. These may be considered representative of all other tellurates as the general shape and peaks observed are about the same. Maximum rates of decomposition were observed at 230, 480, 640 and 1000°C.

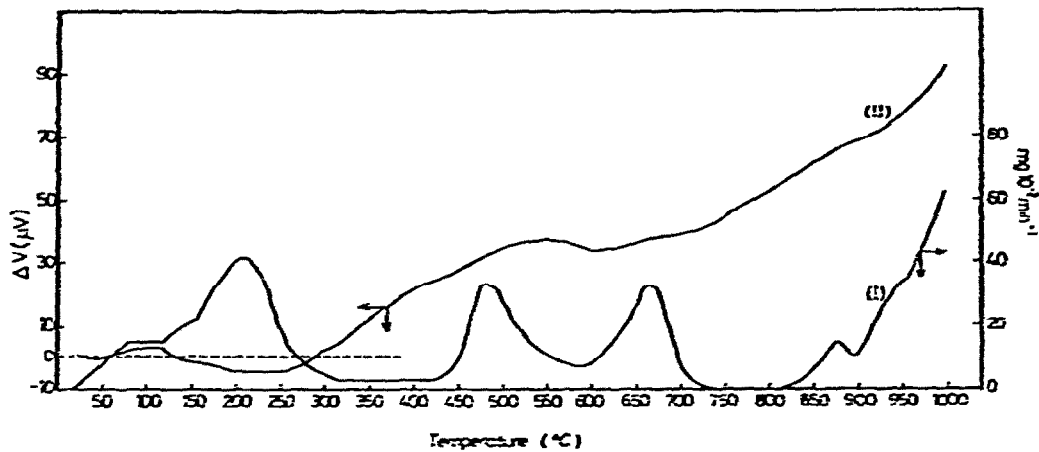The DTA curves do not exhibit sharp peaks. As the loss of oxygen and crystal

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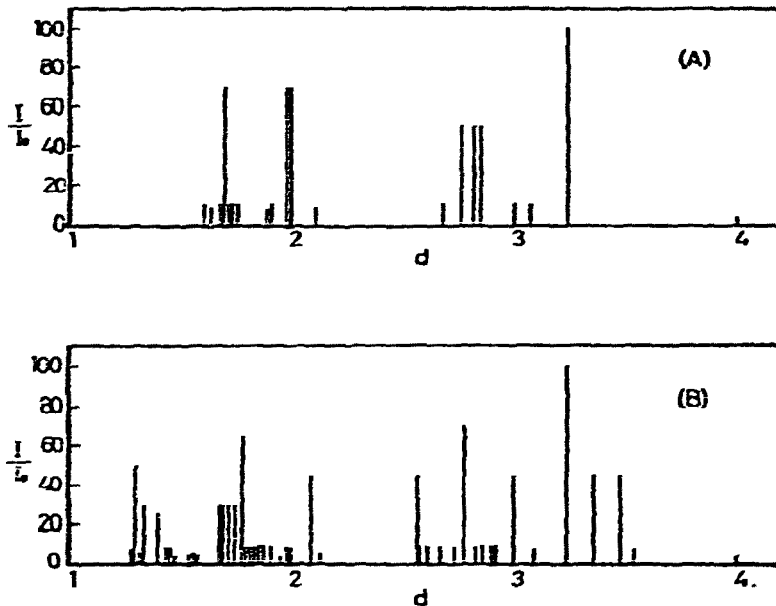Fig. 4. DTG (I) and DTA (II) curves of $Gd_2(TeO_4)_3$. Heating rate = 2°C min⁻¹.

Fig. 5. X-ray diffractograms of lanthanum tellurate heated 4 h at 750°C (A) and 1000°C (B).

re-arrangement are exothermic according to Bart[18], the shape of this curve is not surprising. The small endothermic peak observed at 200–240°C may be due to the loss of about 1/2 TeO_2(or TeO_3) per mole of tellurate already noticed (see Table 4), which corresponds to the peak of the DTG curve. This loss should be endothermic by analogy with selenates[21]. Another possible endothermic effect is noticed at about 600°C which may be related to some transition occurring during the transformation of amorphous to crystalline product, as detected by X-ray diffraction.

X-ray diffraction patterns were obtained for all tellurates and samples taken at points 1, 2 and 3 (Fig. 2). Only samples taken at points 2 and 3 (heated at 750 and

1000°C, respectively) exhibit a crystalline pattern, all the others being amorphous. The patterns given by the A.S.T.M. Joint Committee on Powder Diffraction Standards refer to three lanthanum tellurates ($La_2Te_3O_9$, La_2TeO_6 and $La_2Te_4O_{11}$). However, none of these are similar to the diffractograms obtained with the products described in the present paper and shown in Fig. 5.

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