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SYNTHESIS, CRYSTALLOGRAPHIC DATA AND THERMOSTABILITY OF SOME METAL ORTHO-TELLURATES OF THE TYPE Me_3TeO_6 AND Me_2TeO_6

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ABSTRACT

A method of synthesis of some metal ortho-tellurates of the type Me_3TeO_6 and Me_2TeO_6 was developed. Crystallographic data (parameters of the elementary cell and the number of the formula units of these compounds) were calculated. Their picnometric density and X-ray density were determined and compared. The thermostability of these ortho-tellurates was studied.

INTRODUCTION

Studies of the synthesis of metal ortho-tellurates are rare and literature data may be presented in two groups. Knjazeva et al. [1,2] suggested that metal oxide, elementary tellurium and Na_2CO_3 should be used for the synthesis of ortho-tellurates. The mixture should be homogenized, placed in a furnace (heated to 750–800°C) and heated for 1–2 h. The cake obtained is then leached with a solution of NH_4Cl, thoroughly washed with water and dried. In this way the ortho-tellurates of Zn, Cd and Pb and the ortho-tellurates of the elements from group IIA in the Periodic Table were obtained. Iander and Kienbaum described the synthesis of the ortho-tellurates of copper, silver, mercury and lead [3] by a precipitation reaction of aqueous solutions of the corresponding salts and potassium ortho-tellurate ($K_2H_4TeO_6$). On the basis of experiments they have come to the conclusion that, when a solution of a salt of a heavy metal is mixed with a solution of potassium tellurate, water-containing acidic ortho-tellurates precipitate whose composition is not always reproducible. In some cases, under given conditions, by heating in a water bath in the presence of a residue of the metal ions, the precipitate may become normal ortho-tellurate. The results of the the chemical analysis of the ortho-tellurates reported in ref. 3 differ from the calculated values. This fact makes it reasonable to suppose that the ortho-tel-

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lurates obtained are not stoichiometric compounds, or else they may be a mixture of different phases. The method developed in ref. 2 (leaching of the ortho-tellurate obtained and its further washing with water) can hardly result in a complete removal of the impurities.

This work presents a method of synthesis of metal ortho-tellurates by oxidation of a mechanical mixture of metal oxide and tellurous oxide exactly corresponding to the stoichiometry of the ortho-tellurates obtained. Some of their properties are also presented.

EXPERIMENTAL

Analytical grade metal oxide and tellurous oxide (Merck and Fluka) were used for the synthesis of metal ortho-tellurates. The temperature of initial and intensive oxidation was determined by derivatograph analysis with a Mom derivatograph OD-102 (Hungary). The samples were heated in oxygen, the pressure of the latter being 1 atm., the rate of heating, 150°C h^{-1}, the weight of the initial mixture, 1/1000 mol. The processes leading to the synthesis of metal orthotellurates may be expressed by the equations

$3MeO + TeO_2 + 1/2O_2 = Me_3TeO_6$

$Me_2O_3 + TeO_2 + 1/2O_2 = Me_2TeO_6$

Figures 1 and 2 present the thermogravimetric curves of the temperatures

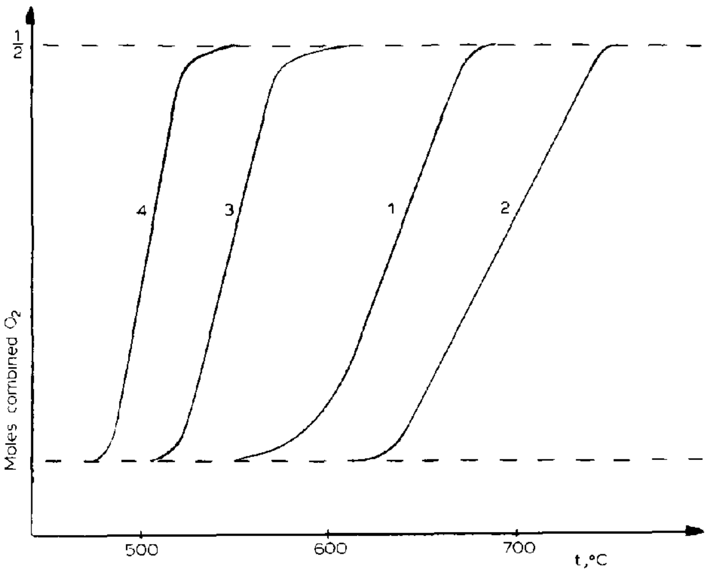

Fig. 1. Thermogravimetric curves of the oxidation of mixtures with composition $3MeO \cdot TeO_2$ in the synthesis of metal ortho-tellurates: (1) Cu_3TeO_6; (2) Zn_3TeO_6; (3) Cd_3TeO_6; (4) Pb_3TeO_6.

of the initial and intensive oxidation leading to the synthesis of metal ortho-tellurates. The maximum quantity of oxygen required for the synthesis of 1 mol of tellurate is 1/2 mol and is also shown in these figures.

The conditions of synthesis of basic bismuth ortho-tellurate having composition $Bi_2O_3 \cdot 2Bi_2TeO_6(Bi_6Te_2O_{15})$ were also studied. Thermogravimetric studies show that oxidation begins at 450–500°C and complete oxidation occurs at 600°C.

Besides the oxidation peaks, the derivatograms of the initial mixtures show the exothermic peaks corresponding to the interaction of metal oxide with tellurous oxide and the synthesis of metal tellurate.

RESULTS AND DISCUSSION

Synthesis of metal ortho-tellurates

Mechanical mixtures were prepared for the synthesis of ten ortho-tellurates, 20-g each, whose composition is shown in Table 1. The mixtures were thoroughly homogenized in an agate mortar, the degree of homogenization being controlled by chemical analysis. The initial mixtures were placed in a corundum crucible and oxidized at temperatures at which the rate of the process is greatest. The heating was accomplished in a crucible furnace which was reconstructed so that a constant pressure of 1 atm was maintained throughout the process. The adjustment and maintenance of the required

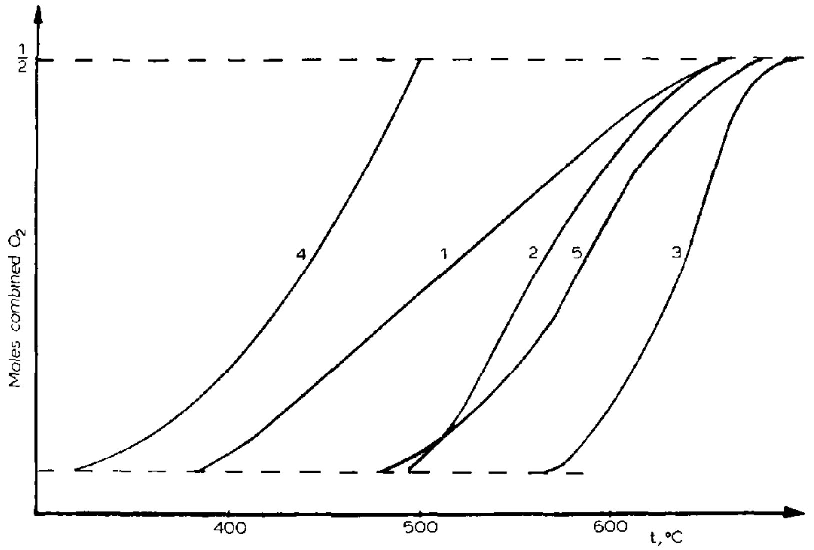

Fig. 2. Thermogravimetric curves of the oxidation of mixtures with composition $Me_2O_3 \cdot TeO_2$ in the synthesis of metal ortho-tellurates: (1) Al_2TeO_6; (2) Ga_2TeO_6; (3) In_2TeO_6; (4) Tl_2TeO_6; (5) Bi_2TeO_6.

temperature were controlled automatically. The steps of the process were: heating of the mechanical mixture for 10 h; cooling; grinding; and twofold oxidation at the same temperatures. The completeness of the oxidation process was checked in two ways.

(1) By a chemical method

The content of both the metal oxide and Te(VI) in the compounds was determined. The content of the metal oxide was determined by direct and reverse complexometric titration [4], and that of Te(VI), iodometrically [5]. The results, calculated and found, are presented in Table 1.

TABLE 1

Chemical analysis of metal ortho-tellurates

Compound	Calcd. (%)		Found (%)	
	MeO (MeO_2; Me_2O_3)	TeO_3	MeO (MeO_2; Me_2O_3)	TeO_3
Cu_3TeO_6	57.61	42.39	57.59	42.35
			57.70	42.40
			57.62	42.38
Zn_3TeO_6	58.16	41.84	58.10	41.90
			58.20	41.82
			58.15	41.85
Cd_3TeO_6	68.69	31.31	68.63	31.33
			68.71	31.20
			68.69	31.30
Al_2TeO_6	36.73	63.27	36.39	63.30
			36.75	63.23
			36.72	63.28
Ga_2TeO_6	51.63	48.37	51.70	48.37
			51.59	48.42
			51.65	48.38
In_2TeO_6	61.26	38.74	61.19	38.75
			61.30	38.70
			61.27	38.75
Tl_2TeO_6	72.23	27.77	72.20	27.69
			72.25	27.83
			72.30	27.78
Pb_3TeO_6	79.22	20.78	79.31	20.75
			79.19	20.83
			79.21	20.79
Bi_2TeO_6	72.63	27.37	72.59	27.39
			72.63	27.35
			72.60	27.36
$Bi_6Te_2O_{15}$	79.92	20.08	80.00	20.03
			79.93	20.10
			79.92	20.05

TABLE 2

Parameters of the elementary cell of the ortho-tellurates studied

Compound	Crystal system	Parameters of elementary cell (Å)				Number of formula units	Literature data parameters (Å)			
		a	*b*	*c*	*β*		*a*	*b*	*c*	*β*
Cu_3TeO_6	cubic	9.536	–	–	–	8	9.537	–	–	–
Zn_3TeO_6	–	–	–	–	–	–	–	–	–	–
Cd_3TeO_6	–	–	–	–	–	–	–	–	–	–
Al_2TeO_6	tetragonal	4.431	–	8.674	–	2	4.445	–	8.70	–
Ga_2TeO_6	tetragonal	4.544	–	8.972	–	2	4.540	–	8.97	–
In_2TeO_6	hexagonal	8.840	–	4.823	–	3	8.860	–	4.82	–
Tl_2TeO_6	trigonal	9.100	–	4.984	–	3	9.070	–	4.98	–
Pb_3TeO_6	monoclinic	7.443	12.024	13.151	125.83	–	7.44	12.02	13.15	125.8
Bi_2TeO_6	orthorhombic	5.315	16.567	5.312	–	4	5.319	16.549	5.318	–
$Bi_6Te_2O_{15}$	orthorhombic	5.682	5.993	5.305	–	4	5.687	5.993	5.307	–

(2) By X-ray analysis

The X-ray patterns of the ortho-tellurates were recorded on a TURM-61M apparatus with Cu K_α emission and a nickel filter for β-emission. The X-ray patterns obtained were compared with those known from the literature. When no data concerning a given ortho-tellurate were available, the purity of the phase obtained was determined by the presence or absence of lines of the initial metal oxide, tellurous oxide or metal tellurite. If no such lines were present the synthesis was considered to be complete and the phase obtained, a pure compound.

Crystallographic studies

On the basis of X-ray patterns the parameters of the elementary cell and the number of formula units in it were calculated. The results are shown in Table 2. All lines of the X-ray patterns belong to the corresponding elementary cell. No lines of the initial metal oxide, tellurous oxide or metallic tellurte were recorded. The parameters of the ortho-tellurates under study are also in good agreement with the literature data which confirms the accuracy of the chemical analyses and the identity of the ortho-tellurates obtained here.

Density

Density was determined picnometrically in tetrachloromethane according to the technique reported in ref. 6. X-ray density was also calculated. The data in Table 3 show that the calculated and found densities of the ortho-tellurates under study are in good agreement.

TABLE 3

Density of some metal ortho-tellurates (g cm^{-3})

No.	Compound	Found	Calcd. (X-ray)
1	Cu_3TeO_6	6.34	6.36
2	Zn_3TeO_6	–	–
3	Cd_3TeO_6	–	–
4	Al_2TeO_6	5.32	5.37
5	Ga_2TeO_6	6.51	6.52
6	In_2TeO_6	6.90	6.92
7	Tl_2TeO_6	8.91	8.88
8	Pb_3TeO_6	–	–
9	Bi_2TeO_6	9.07	9.09
10	Bi_6TeO_{15}	8.90	8.91

Thermal dissociation

The thermal dissociation of metal ortho-tellurates was studied on a derivatograph (Paulik–Paulik–Erdey, MOM) in air, at a heating rate of 10° min^{-1}, with a sample weight of 600–1000 mg.

Figure 3A shows that copper ortho-tellurate is thermostable to 810°C. Zn_3TeO_6 (Fig. 3B) also exhibited high thermostability in the temperature interval under study (to 930°C). The insignificant increase in sample weight (~ 0.3 wt%) observed at 700–800°C is due to the presence of unoxidized tellurite which is oxidized under these conditions. In the sample, which has been further oxidized, these effects are absent. Therefore, derivatograph analysis may also be used to prove the completeness of oxidation of the initial mixture of tellurite and oxide. In the case of Cd_3TeO_6 (Fig. 3C), there are two endothermic peaks (353 and 750°C) associated with non-intensive weight losses (0.21 and 0.14 wt%, respectively) which are probably due to a process of reduction. The endothermic peak observed at 661°C on the DTA curve of Al_2TeO_6 (Fig. 3D) probably corresponds to the melting of traces of an unoxidized phase which is a mixture of $Al_2(TeO_3)_3$ and Al_2O_3 with a composition similar to the eutectic. The melting point of this composition

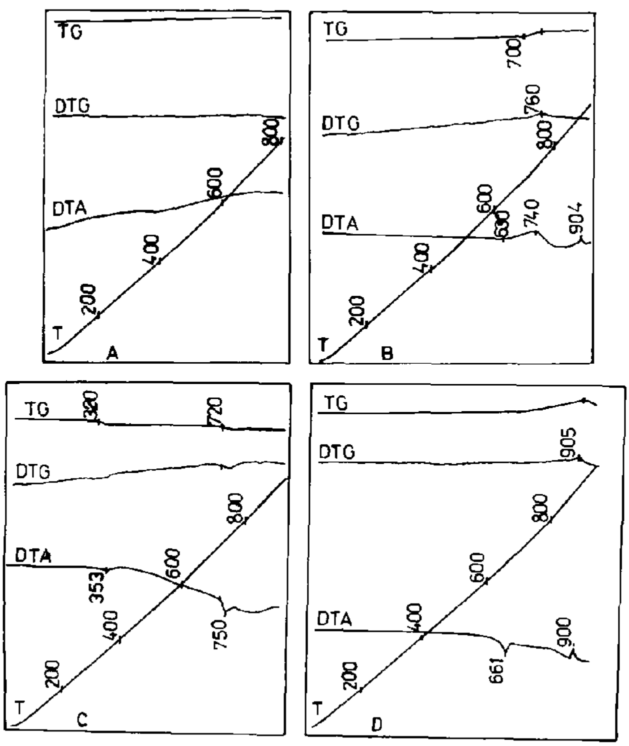

Fig. 3. Derivatograms: (A) Cu_3TeO_6; (B) Zn_3TeO_6; (C) Cd_3TeO_6; (D) Al_2TeO_6.

according to literature data is 680°C [7]. The increase of the sample weight observed at 640–917°C accompanied by an exothermic peak is due to the oxidation of these particular phases, since in the samples that were oxidized further there are no thermal peaks in the interval to 920°C.

Figure 4A presents the derivatogram of Ga_2TeO_6. The compound is thermostable to 850°C. At 870–990°C a complete dissociation of tellurate to tellurite and further dissociation of the latter takes place. The weight loss is 5 wt% while the calculated weight loss for the transition tellurate–tellurite is 2.2 wt%.

In_2TeO_6 (Fig. 4B) has a higher thermostability than Ga_2TeO_6. Insignificant dissociation is observed above 900°C, but even at 1000°C, where the weight loss is 0.23 wt%, complete dissociation is not attained. The lowest thermostability for the IIIA group belongs to Tl_2TeO_6 (Fig. 4C). As its TG curve shows its dissociation in air starts at lower temperatures compared with dissociation in oxygen since the partial pressure of oxygen in air is as low as 152 mm Hg. The initial temperature of dissociation is 570°C but the maximum rate of dissociation occurs at 600°C. In oxygen medium, at a pressure of 1 atm, thermogravimetric studies show that at 630°C, i.e., long before the melting point, Tl_2TeO_6 partially loses oxygen. Above 650°C it

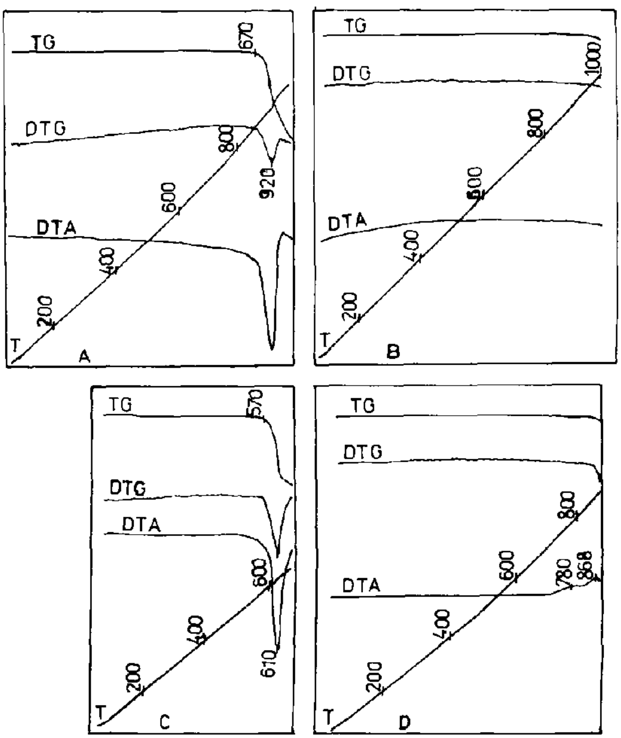

Fig. 4. Derivatograms: (A) Ga_2TeO_6; (B) In_2TeO_6; (C) Tl_2TeO_6; (D) Pb_3TeO_6.

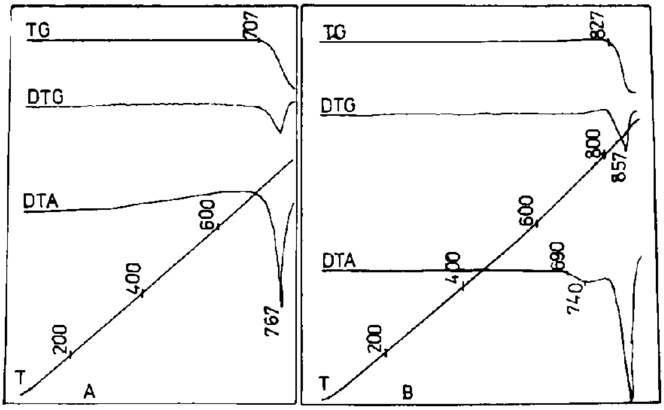

Fig. 5. Derivatograms: (A) Bi_2TeO_6; (B) $Bi_6Te_2O_{15}$.

melts and dissociaties completely and volatile substances are released. The result is a complex mixture of phases not yet clearly identified but belonging to the system Tl_2O–Tl_2O_3–Te_2O_2. Figure 4D presents the thermogram of Pb_3TeO_6. The dissociation of ortho-tellurate to oxotellurite starts at 730°C. The process is very complicated since dissociation occurs parallel to oxidation, which is due to the equilibrium tellurite–tellurate being established [8]. At 870°C ortho-tellurate starts to dissociate along with oxidation.

The conclusions of Knjazeva et al. [2] that Pb_3TeO_6 starts to dissociate as early as at 200°C are not correct. The derivatograms reported show that no ortho-tellurate dissociates at such a low temperature. The peaks recorded by these authors of the liberation of hygroscopic moisture at 150°C, the melting of $PbTeO_3$ at 575°C, and the endothermic peak at 870°C associated with the melting of PbO, are probably due not to the formation of PbO and $PbTeO_3$ resulting from the dissociation of Pb_3TeO_6, but to impurities of these compounds in the sample to be heated. Figure 5A shows the derivatogram of Bi_2TeO_6. It is stable up to 700°C. At 750°C it dissociates intensively to form Bi_2TeO_5, when O_2 is released. The second bismuth ortho-tellurate, $Bi_6Te_2O_{15}$, is more thermostable. A minor endothermic peak is observed on the DTA curve at 740°C, which is probably connected with a certain reconstruction of the crystal lattice. As the TG curve shows, no weight loss of the initial sample is observed at this temperature. At 827°C the compound dissociates to form basic bismuth tellurite and O_2 is liberated.

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