Synthesis and Characterisation of New Mixed Oxides of Antimony and Tellurium†

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Two mixed oxides of antimony and tellurium, of composition $Sb_2Te_2O_9$ and Sb_2TeO_7, have been synthesised by the solid-state reaction of TeO_2 and Sb_2O_3 or Sb_2O_5. Single crystals of $Sb_2Te_2O_9$ have been obtained by transport processes. The crystallographic constants of these compounds have been determined by *X*-ray diffraction methods. Their i.r. absorption spectra are very similar and frequencies corresponding to the E–O–E (E = Sb or Te) vibrations have been assigned. The thermal decomposition of these oxides, at temperatures above 950 °C, leads to Sb_2O_4 as the only solid phase.

For some years we have been studying the synthesis and chemical behaviour of mixed oxides of semi-metallic elements. To date, a series of mixed oxides of selenium and tellurium have been isolated and characterised,[1,2] selenium and tellurium being adjacent elements in the same Group in the Periodic Table (Group 6B). Following from this work, a line of research which suggests interesting possibilities is the study of the preparation and characterisation of mixed oxides of elements belonging to neighbouring Groups in the Periodic Table. Here the similarity of ionic radii (much greater, in general, than between elements belonging to the same group) favours mutual substitution, similar structural units and co-ordination being maintained, while, at the same time, lattice defects necessary for the accommodation of defect or excess charges produced by substitution can be introduced.

Antimony and tellurium are an example of typical semi-metallic elements belonging to neighbouring Groups and thus it was thought that the study of systems where both intervene would probably lead to the isolation of mixed compounds possessing characteristics intermediate to those of the precursor species.

The tendency of antimony to form mixed oxides with a large number of elements in the Periodic Table and especially with alkali, alkaline-earth, and transition metals is well known.[3] On the other hand, oxygenated antimony compounds with elements of a semi-metallic nature have been much less frequently studied. The synthesis of an antimony tellurite, of formula $Sb_2(TeO_2)_3 \cdot 5H_2O$, by reaction in solution between $Na_2(TeO_3)$ and $SbCl_3$ has been described.[4] The thermal decomposition of this hydrated species gives rise to $Sb_2(TeO_3)_3$ which can also be obtained directly by oxidation of Sb_2Te_3 at 350—405 °C.[5]

The present paper describes the preparation of new mixed oxides of antimony and tellurium in the form of single crystals and microcrystalline powders, together with their characterization by chemical analysis, *X*-ray powder diffraction, thermogravimetric analysis, and infrared spectroscopy.

Experimental

Sb_2O_5 was obtained by hydrolysis of $SbCl_5$[6] in the form of a yellow microcrystalline powder, which was identified by chemical analysis (Found: Sb, 74.5. Calc.: Sb, 75.25%) and *X*-ray powder diffraction. Sb_2O_4, a pale yellow powdery solid, was synthesised by heat-treating Sb_2O_3 (Carlo Erba R.P.E.) in air at 600 °C for 24 h. The product was identified by *X*-ray diffraction and chemical analysis (Found: Sb, 78.3. Calc.: Sb, 79.20%). TeO_3 was synthesised from $Te(OH)_6$ (AnalaR B.D.H.) by heating at 350 °C for 24 h. The product so obtained was pale yellow, amorphous to *X*-rays, and its composition established by the loss of weight of the $Te(OH)_6$ starting material and by chemical analysis (Found: Te, 72.3. Calc.: Te, 72.65%). Te, TeO_2, and Sb were supplied by Merck (RPA).

The mixed oxides of antimony and tellurium were obtained by solid-state reactions on heating intimate mixtures of the finely divided reactants at different temperatures up to 800 °C in porcelain crucibles and in Pyrex or quartz capsules with an initial static vacuum of 10^{-3} mmHg. Mixtures of TeO_3 + Sb_2O_3, TeO_3 + Sb, TeO_2 + Sb_2O_5, TeO_2 + Sb_2O_4, TeO_2 + Sb_2O_3, Te + Sb_2O_5, and Te + Sb_2O_3 in various initial proportions were treated under the above conditions. After the reaction time had been completed, the process was stopped by extracting the crucibles from the furnace or by immersing the capsules in liquid nitrogen.

Single crystals of the oxide $Sb_2Te_2O_9$ were obtained by introducing a mixture of TeO_2 and Sb_2O_5 (1.5 g) in a 2:1 molar ratio, together with $TeCl_4$ (50 mg), in a quartz capsule (30 cm long and 12 mm internal diameter), which was then evacuated to 10^{-3} mmHg and sealed. The capsule was placed in a transport furnace for 5 d in the temperature gradient 700—750 °C. The capsule was then cooled in the furnace at a rate of 50 °C h^{-1}. Using the same conditions it was also possible to prepare single crystals of $Sb_2Te_2O_9$ from a microcrystalline powder of the same compound and using $TeCl_4$ as the transport agent.

The products obtained were characterised by chemical analysis, using a modification to the methods described in the literature. The samples, which are insoluble in acids or alkaline solutions, were decomposed in fused KOH by heating for 15 min in a nickel crucible. The fused mass, after cooling, was dissolved in distilled water followed by neutralization with HCl. Tellurium analysis was carried out gravimetrically by reduction to elemental Te with Na_2SO_3.[7] Antimony analysis was performed by reduction to elemental Sb with a Cr^{2+} solution in 3 mol dm^{-3} hydrochloric acid. Under these conditions, Sb and also the Te present in the solution are precipitated. Weighing the precipitate gave the total content of Sb + Te in the sample. By subtracting the previously determined tellurium percentage, the antimony content could thus be obtained. The oxygen content was deduced by difference.

X-Ray diffraction diagrams were obtained by the powder method using a Siemens D500 generator and Cu-K_α radiation. The diffractograms were determined using a goniometric velocity of 1° min^{-1} and Si was the internal standard.

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† *Non-S.I. unit employed:* mmHg ≈ 13.6 × 9.8 Pa.

A preliminary crystallographic study of $Sb_2Te_2O_9$ was carried out using an Enraf-Nonius CADLF automatic four-circle single-crystal diffractometer controlled by a Digital PDP 8-A computer. Mo-K_α radiation was used after being rendered monochromatic by a graphite crystal. The reciprocal space of a selected single crystal was explored systematically until a total of 25 reflections had been obtained. The matrix orientation was calculated and the Miller indices of the reflections assigned. The diffraction angles determined were refined by a least-squares method (refinement of lattice constants by least squares, Institute of Crystallography, University of Freiburg, Germany).

Electron-diffraction diagrams and micrographs were obtained using a high-resolution Siemens Elmiskop 102 electron microscope equipped with a goniometric grid holder capable of double inclination (up to ± 45°) and 2-mm vertical displacement. The working voltage was always 100 kV.

Density measurements were carried out by the picnometric method for solids with CCl_4 as the picnometric liquid.

Thermogravimetric (t.g.) and differential thermogravimetric (d.t.g.) curves were determined with a TG50 balance attached to a Mettler TA3000 thermal analyser equipped with a TC10 processor unit.

The infrared spectra were recorded on a Perkin-Elmer 325 spectrophotometer. The samples were diluted with 95% KBr.

Results and Discussion

No mixed phase was obtained by heat-treating mixtures of TeO_3, Sb, or Te; only mixtures of the starting reactants and their decomposition products were identified. However mixed oxides of antimony and tellurium, in oxidation states V and VI respectively, were prepared from mixtures containing tellurium dioxide. Table 1 summarises the treatment conditions and the products identified by *X*-ray powder diffraction. The reaction time was 24 h in all cases.

The reaction between TeO_2 (paratellurite) and Sb_2O_3 (valentinite) at temperatures below 700 °C in air yields only mixtures of TeO_2 and Sb_2O_3 or Sb_2O_4 depending on the temperature. At 700 °C the *X*-ray powder diffraction diagram registers the appearance of a series of additional lines corresponding to a new phase which could be isolated pure when the molar ratio of the initial oxide mixture was 2.6:1. This product is a yellowish white microcrystalline solid whose composition, obtained by chemical analysis (Table 2), is $Sb_2Te_2O_9$. The proximity of the temperature at which this compound forms to the sublimation temperature of TeO_2 make the addition of a slight excess of this reactant over the stoicheiometric amount necessary in order to complete the process.

Figure 1 shows the t.g. and d.t.g. curves for the thermogravimetric analysis of a mixture of TeO_2 and Sb_2O_3 in a 2:1 molar ratio. The heating rate was 2 °C min^{-1} in air. At temperatures above 700 °C the new phase $Sb_2Te_2O_9$ was identified by *X*-ray powder diffraction. The reaction to form this oxide takes place in two successive steps. In the first, a gain in weight is observed which can be attributed to the oxidation of Sb_2O_3 to Sb_2O_4 by oxygen from the air. Indeed *X*-ray diffraction diagrams of the mixture after the first step show the presence of mixtures of TeO_2 and Sb_2O_4 (paratellurite and cervantite, respectively). The second step consists of a further oxidation process which occurs simultaneously with the formation of the mixed oxide, after which all the antimony exists in oxidation state V. These facts seem to suggest that the reaction occurs, in reality, between Sb_2O_4 and TeO_2, and carrying out the experiment under the same conditions using these compounds as the starting reactants does indeed yield the same product (Table 1).

The presence of oxygen seems to be a determining factor in the formation of the mixed oxide, as reactions carried out in evacuated capsules under the same conditions give rise to mixtures in which Te and Sb_2O_4 are identified, Te arising from the reduction of TeO_2 by Sb_2O_3.

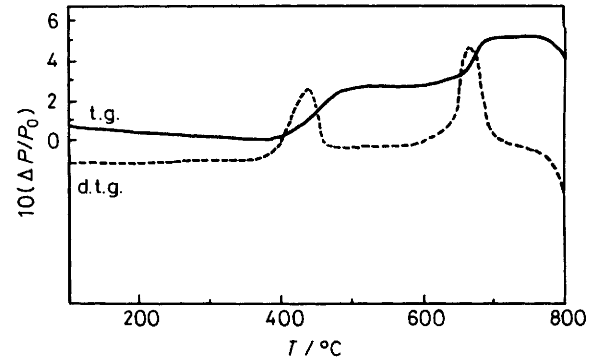

Figure 1. T.g. and d.t.g. curves for a TeO_2 and Sb_2O_3 oxide mixture with a 2:1 molar ratio. Heating rate is 2 °C min^{-1}

Table 1. Initial proportions, treatment conditions, and products identified in the reactions between TeO_2 and Sb_2O_3, Sb_2O_4, or Sb_2O_5

Reactants	Molar ratio	Treatment conditions (°C)	Products identified
$TeO_2 + Sb_2O_3$	4:1, 3.5:1, 3:1	700, air	$Sb_2Te_2O_9$, TeO_2
	2.6:1	700, air	$Sb_2Te_2O_9$
	2:1, 1:1	700, air	$Sb_2Te_2O_9$, Sb_2O_4
	4:1, 2:1, 1:1	650, 800, vacuum	Te, Sb_2O_4
$TeO_2 + Sb_2O_4$	2.6:1	700, air	$Sb_2Te_2O_9$
$TeO_2 + Sb_2O_5$	4:1	500, 600, air, vacuum	$Sb_2Te_2O_9$, TeO_2
	2:1	500, 600, air, vacuum	$Sb_2Te_2O_9$
	1:1	600, air, vacuum	$Sb_2Te_2O_9$, Sb_2O_4
	1:1	700, vacuum	Sb_2TeO_7

Table 2. Chemical analysis of $Sb_2Te_2O_9$ and Sb_2TeO_7

	Sb (%)		Te (%)		O (%)	
Compound	Found	Calc.	Found	Calc.	Found	Calc.
$Sb_2Te_2O_9$	37.6	37.85	39.5	39.70	22.9	22.40
Sb_2TeO_7	50.9	50.40	26.5	26.40	22.6	23.20

Table 3. Experimental and calculated *d* spacings (Å), relative intensities, and Miller indices for $Sb_2Te_2O_9$ and Sb_2TeO_7

$Sb_2Te_2O_9$				Sb_2TeO_7			
hkl	$d_{calc.}$	$d_{exp.}$	I/I_0	*hkl*	$d_{calc.}$	$d_{exp.}$	I/I_0
001	13.759	13.64	7	200	7.163	7.16	10
200	10.370	10.31	5	110	6.674	6.69	12
$\bar{2}02$	6.900	6.92	2	210	5.194	5.20	7
$\bar{3}02$	5.970	5.97	13	202	4.542	4.543	22
400	5.160	5.16	3	310	4.035	4.052	32
202	4.994	5.011	4	212	3.891	3.900	62
011	4.583	4.585	2	103	3.777	3.786	6
$\bar{2}11$	4.375	4.375	9	120	3.647	3.667	8
$\bar{5}02$	4.223	4.220	8	021	3.591	3.600	18
$\bar{1}12$	4.047	4.040	3	121	3.483	3.531	100
$\bar{2}12$	3.973	3.978	2	113	3.377	3.394	66
$\bar{4}11$	3.635	3.633	7	220	3.337	3.335	26
$\bar{6}02$	3.600	3.597	14	410	3.236	3.249	13
$\bar{4}10$	3.537	3.538	100	221	3.210	3.288	16
212	3.483	3.477	22	122	3.098	3.096	28
600	3.439	3.440	8	320	2.960	2.975	19
411	3.249	3.226	40	222	2.901	2.912	92
$\bar{5}12$	3.188	3.184	22	500	2.866	2.867	9
$\bar{5}10$	3.145	3.140	55	014	2.736	2.745	22
601	3.098	3.081	4	114	2.688	2.694	38
$\bar{5}13$	2.976	2.976	4	511	2.612	2.614	50
700	2.947	2.935	2	421	2.536	2.531	8
412	2.885	2.887	47	413	2.494	2.492	29
$\bar{6}10$	2.807	2.804	8	130	2.476	2.472	32
602	2.728	2.730	16	600	2.388	2.401	27
$\bar{7}12$	2.624	2.621	5	230	2.372	2.368	9
800	2.579	2.576	3	005	2.349	2.351	12
413	2.531	2.536	2	124	2.287	2.295	9
$\bar{7}10$	2.520	2.496	4	602	2.212	2.213	7
020	2.430	2.427	14	215	2.140	2.150	7
$\bar{8}12$	2.385	2.383	5	332	2.081	2.074	36
				006	1.956	1.954	15
				333	1.934	1.934	10
				415	1.901	1.899	7
				140	1.870	1.870	6

Reactions between TeO_2 and Sb_2O_5 yield $Sb_2Te_2O_9$ at a lower temperature, 500 °C, when carried out both in air and in vacuum. However, when the molar ratio of the starting oxide mixture is 1 : 1 the formation of a new crystallographic phase is observed at 700 °C in vacuum. The diffraction lines of this phase do not coincide with any known oxide of tellurium or antimony. This product is a yellowish microcrystalline powder whose composition, determined by chemical analysis (Table 2) is Sb_2TeO_7.

In the oxides $Sb_2Te_2O_9$ and Sb_2TeO_7 tellurium can be taken as being in oxidation state IV as in general oxygenated compounds of Te^{VI} are unstable at temperatures above 500—600 °C, while these compounds are stable above 750 °C. Taking this into account, together with the compositions derived from chemical analysis, antimony must be in oxidation state V. This result is consistent with the fact that, in the case of $Sb_2Te_2O_9$, the synthesis starting from Sb_2O_5 takes place at a considerably lower temperature than when starting from Sb_2O_3, which is possibly due to oxidation of antimony by air being unnecessary in the former case.

The methods used to synthesise the new phases detailed so far lead to their obtention in the form of a microcrystalline powder. It has also been possible to prepare $Sb_2Te_2O_9$ as single crystals by means of transport processes in evacuated capsules using $TeCl_4$ as the transport agent. The crystals produced are yellow, needle shaped and appear adhering to the walls of the cold zone of the capsule. *X*-Ray diffraction diagrams of the powder obtained by grinding the single crystals are analogous to those from the microcrystalline powder prepared as already described.

A preliminary single-crystal *X*-ray crystallographic study of $Sb_2Te_2O_9$ was carried out. The compound belongs to the monoclinic system, space group $P2_1/c$, with a = 21.921(8), b = 4.8667(9), c = 14.609(5) Å, β = 109.75(3)°, U = 1 465.1(5) Å^3, D_m = 5.9 g cm^{-3}, Z = 8, D_c = 5.83. A crystallographic study of Sb_2TeO_7 was performed by analysing its *X*-ray powder diffraction pattern. The compound possess an orthorhombic type of symmetry, with a *Pmmm* space group and with a = 14.327, b = 7.542, c = 11.745 Å, U = 1 269.3 Å^3, D_m = 5.1 g cm^{-3}, Z = 8, D_c = 5.06, g cm^{-3}.

Table 3 presents the *d* spacings and relative intensities of the reflections observed in the *X*-ray powder diffraction patterns of $Sb_2Te_2O_9$ and Sb_2TeO_7. The Miller indices were assigned using the previously determined lattice parameters.

An electron microscopic study on both Sb_2TeO_9 and Sb_2TeO_7 showed that they consist of single phases formed from crystals of a homogeneous aspect. All the electron-diffraction diagrams could be interpreted from the parameters deduced from *X*-ray diffraction. No additional reflections, which might indicate the presence of long-range order in the crystal, were detected.

The thermal decomposition of $Sb_2Te_2O_9$ and Sb_2TeO_7 in air was studied using a heating rate of 2 °C min^{-1}. The t.g. and d.t.g. curves are shown in Figure 2. Similar behaviour can be seen in both cases. $Sb_2Te_2O_9$ is stable, under the conditions studied, up

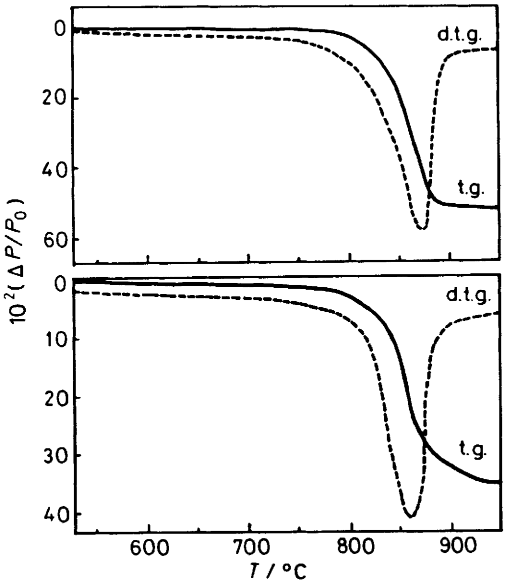

Figure 2. T.g. and d.t.g. curves for (*a*) $Sb_2Te_2O_9$ and (*b*) Sb_2TeO_7. Heating rate is 2 °C min^{-1}

to 770 °C at which temperature it starts to decompose with a 52.6% weight loss. This continues up to 900 °C when the process is complete. Similarly Sb_2TeO_7 decomposes at temperatures above 760 °C, losing 35.8% in weight in total. β-Sb_2O_4 was identified by *X*-ray powder diffraction and chemical analysis as the only product present in the residue from both decomposition reactions. Thus the decomposition reactions of both oxides take place by the elimination of $TeO_2(g)$ and $O_2(g)$ according to equations (1) and (2).

$$Sb_2Te_2O_9(s) \longrightarrow 2TeO_2(g) + \tfrac{1}{2}O_2(g) + Sb_2O_4(s) \quad (1)$$

$$Sb_2TeO_7(s) \longrightarrow TeO_2(g) + \tfrac{1}{2}O_2(g) + Sb_2O_4(s) \quad (2)$$

The elimination of $TeO_2(g)$ and $O_2(g)$ must be practically simultaneous as the d.t.g. curve shows no discontinuity or splitting which might indicate the superposition of successive processes. The calculated weight losses for the processes referred to are 52.16 and 36.35% respectively, which are in reasonable agreement with the experimental values.

The infrared absorption spectra of both Sb_2TeO_9 and Sb_2TeO_7 show great similarities. It has not been possible to assign the bands by an analysis of the group frequencies, as the crystalline structure of these compounds is not known. Thus assignments have been made by comparison with species of similar characteristics. The absorption spectra of some metallic antimonates are well known, especially those of composition M^ISbO_3 and $M^{II}Sb_2O_6$.[9,10] In all these compounds antimony(V) exhibits six-fold co-ordination, the octahedra are linked by sharing their vertices to form two- or three-dimensional macroanions of the $[SbO_3]^-$ type. This behaviour seems to be general, being observed not only in metallic antimonates, but also in a large number of Sb^V compounds [for example, Sb_2O_5, $Sb(OH)_6^-$, *etc.*].

Thus it would not seem unreasonable to suppose that polyanions of the type $[SbO_3]^-$ just described should also exist in tellurium and antimony oxides. Accordingly the vibrational frequencies of the Sb–O, Sb–O–Sb, and O–Sb–O bonds in the mixed oxides will be comparable to those described in the literature for the previously mentioned compounds. The assignment of the vibrational frequencies corresponding to the Te–O, Te–O–Te, and O–Te–O bonds has been made by comparison with those described in the literature for some oxygenated compounds of Te^{IV} such as metallic tellurites, TeO_2, tellurium sulphate, *etc.*[11,12]

Table 4. I.r. frequencies (cm^{-1}) and assignments for $Sb_2Te_2O_9$ and Sb_2TeO_7

$Sb_2Te_2O_9$	Sb_2TeO_7	Assignment
893		Combination
880		
845	855	
	800	ν(Sb–O) + ν(Te–O)
785	780	
758		
740	735	
	715	
700	697	ν(Sb–O–Sb) + ν(Te–O–Te)
680		
650	652	
635	625	
550	562	
527		ν(Te–O–Sb)
500	518	
460	467	ν(Te–O–Te)
	440	
410	413	
365		δ(O–Sb–O) + δ(O–Te–O)
335	335	
305	305	
265	260	
245	250	δ(O–Te–O) + Lattice vibrations
230		

Table 4 gives the frequencies of the absorption bands of $Sb_2Te_2O_9$ and Sb_2TeO_7 together with their respective assignments. The region between 800 and 715 cm^{-1} relates to the stretching vibrations of the Sb–O and Te–O bonds, as is observed in a large number of antimonates such as $LiSbO_3$ (720 cm^{-1}), $Ni_2Sb_2O_6$ (725 cm^{-1}) and in $(Te_2O_3)SO_4$ (770, 720 cm^{-1}) and TeO_2 (780 cm^{-1}). The wide frequency zone between 700 and 400 cm^{-1} corresponds to the vibrations of the element–oxygen–element bonds. Between 700 and 550 cm^{-1} the ν(Te–O–Te) and ν(Sb–O–Sb) vibrations are superposed and so the assignment of particular bands is arbitrary. On the other hand, in the 490—410 cm^{-1} region the ν(Te–O–Te) vibrations are typically seen, as occurs in $HNO_3{\cdot}2TeO_2$ (490, 438 cm^{-1}) and $(Te_2O_3)SO_4$ (460, 435 cm^{-1}). The well defined bands at 527 and 500 cm^{-1} for $Sb_2Te_2O_9$ and at 518 cm^{-1} for Sb_2TeO_7 have been assigned to the ν(Te–O–Sb) stretching vibrations, which must lie between those of ν(Te–O–Te) and ν(Sb–O–Sb). Lastly, the lowest frequency region of the spectra corresponds to the deformation vibrations of the oxygen–element–oxygen bonds as is observed in $Ba_2Sb_2O_6$ [δ(SbO_2) 320, 260 cm^{-1}], $KSbO_3$ [δ(SbO_2) 330, 275 cm^{-1}], TeO_2 [δ(TeO_2) 330, 270 cm^{-1}], and $HNO_3{\cdot}TeO_2$ [δ(TeO_2) 350, 310 cm^{-1}]. At lower frequencies the TeO_2 vibrations appear superimposed on lattice vibrations.

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