

SYNTHESES OF MIXED OXIDES OF THE SYSTEM

Te(VI)–Sb(V)–M(I) (M(I) = Ag, Tl, K, Rb, Cs)

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ABSTRACT

The synthesis of mixed oxides of composition $M^I(Sb^V Te^{VI})O_6$ ($M^I = Ag, Tl, K, Rb, Cs$) with a pyrochlore cubic structure (space group $Fd3m$, No. 227), has been performed at low temperatures starting from $Te(OH)_6$, Sb_2O_3 and the respective metallic nitrates for all the M^I . The stages of the processes have been studied from the TG and DSC curves and the four main stages of the overall reaction are interpreted. Finally, refined crystallographic data have been supplied for the reticular parameters of the five oxides obtained.

INTRODUCTION

The mixed oxides of stoichiometry $A_2B_2O_7$ and $A_2B_2O_6$ with the pyrochlore structure (space group $Fd3m$, No. 227) are of singular importance as a result of their interesting structural aspects and their wide applications. The structural features of pyrochlore-type compounds have been extensively examined [1,2], above all in regard to the distribution of cations A and B in the oxygen framework. The technological applications of these materials are chiefly derived from their magnetic properties, in catalysis, and their growing use in the field of electronics [3–5].

The usual methods of preparation of this wide range of compounds consist generally in ceramic treatments at temperatures above 800–900 °C of the binary metal oxides of the elements involved or some oxosalts (such as nitrates, carbonates, etc.), often followed by annealing of the product at high temperature.

Previous experience in the field of the semimetallic elements has shown that Te and Sb present a peculiar stereochemical behaviour in low oxidation states [6–9], and also it is well known that in their maximum degrees of valence (Te(VI) and Sb(V)), these elements form mixed oxides structurally related to some of the heaviest elements in the 6 and 5 groups of transition metals, respectively [10–12].

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Many oxoderivatives of tellurium can be obtained in gentle thermal conditions starting from "orthotelluric" acid [13,14], $\text{Te}(\text{OH})_6$, which is dehydrated in successive steps, giving place to amorphous TeO_3 and finally to TeO_2 (tetragonal form) at temperatures close to 600°C , in various progressive stages of reduction. But these reduction processes are frequently inhibited in the presence of metallic oxides, even at very high temperatures, and mixed oxides of $\text{Te}(\text{VI})$ have been observed at temperatures of nearly 900°C .

This study describes the main transformations recorded in the course of the processes of thermal decompositions in air of mixtures of commercially available reagents $\text{Te}(\text{OH})_6$, Sb_2O_3 and nitrates of monovalent metals, which leads to isolation of the corresponding mixed oxides $\text{M}^1(\text{SbTe})\text{O}_6$ with pyrochlore structure. Some of them, for example $\text{Ag}(\text{SbTe})\text{O}_6$, have only been obtained through reaction in solution (by ionic exchange). The previously reported crystallographic data [15–17], have been refined in this work. The synthesis processes performed produced the mixed oxides at relatively low temperatures as unique solid-phases, whose crystallinity can be increased after successive annealings at the treatment temperature.

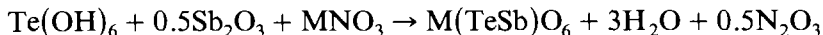
EXPERIMENTAL

The starting reagents, orthotelluric acid, antimony trioxide and metal nitrates, were supplied by Merck (F.R.G.), p.a. quality. The thermogravimetric (TG) and differential scanning calorimetry (DSC) curves were obtained with a Mettler thermal analyzer TA-3000. The experiments were carried out in air using 25 mg samples with a heating rate of 5°C min^{-1} . X-ray diffraction patterns were registered with a Siemens Kristalloflex powder diffractometer powered by a D-500 generator (W has been used as internal standard) and using filtered $\text{Cu } K_\alpha$ radiation.

RESULTS AND DISCUSSION

Figure 1 shows the TG curves of the five initial mixtures of $\text{Te}(\text{OH})_6$, Sb_2O_3 and MNO_3 ($\text{M} = \text{Tl}, \text{Ag}, \text{K}, \text{Rb}$ and Cs) in molar ratios 1:0.5:1, heated to 750°C . Figure 2 represents the DSC curves of these same reagents, recorded up to 600°C , the upper limit of the available technique. These graphs have been arranged in order of increasing melting point (labelled as MP in Fig. 1) of the respective monovalent metal nitrates, in order to appreciate their influence on the course of the reaction.

The overall processes recorded can be conventionally summarized as



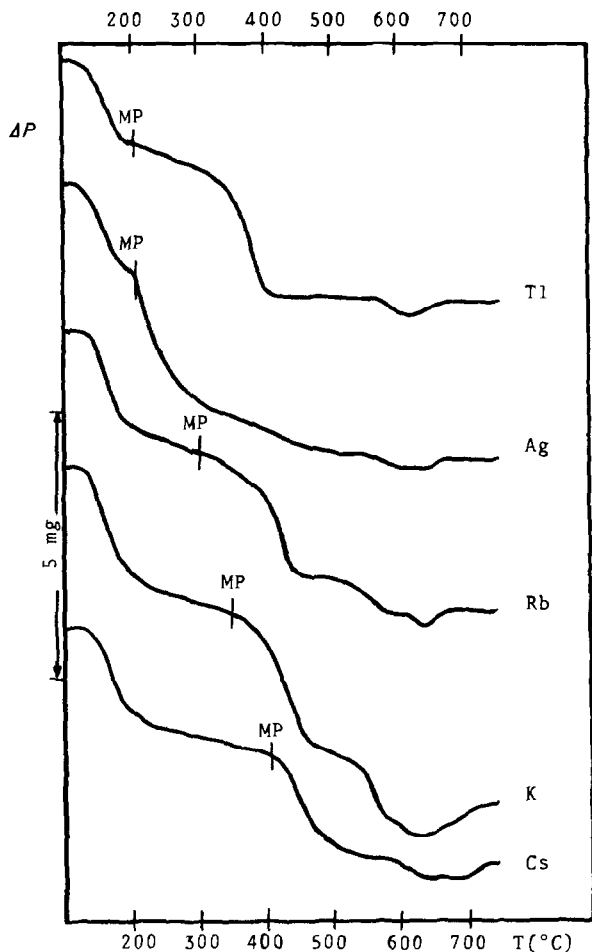
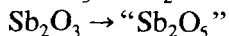
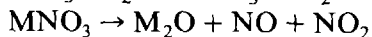
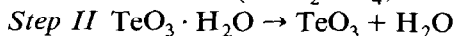


Fig. 1. TG curves of the reactants $\text{Te}(\text{OH})_6$, Sb_2O_3 , MNO_3 ($M = \text{Tl}, \text{Ag}, \text{Rb}, \text{K}, \text{Cs}$). (MP denotes the melting point of MNO_3 .)

Starting from the evolution observed in the thermograms it is possible to differentiate four reaction steps for systematizing the transformations according to the following scheme



Partial dehydration of orthotelluric acid to give the amorphous hydrated tellurium trioxide (or H_2TeO_4 , "metatelluric acid").



Formation of $\alpha\text{-TeO}_3$, also amorphous to X-ray, concomitant in general with the decomposition of the metal nitrate (which lost nitrogen oxides), and

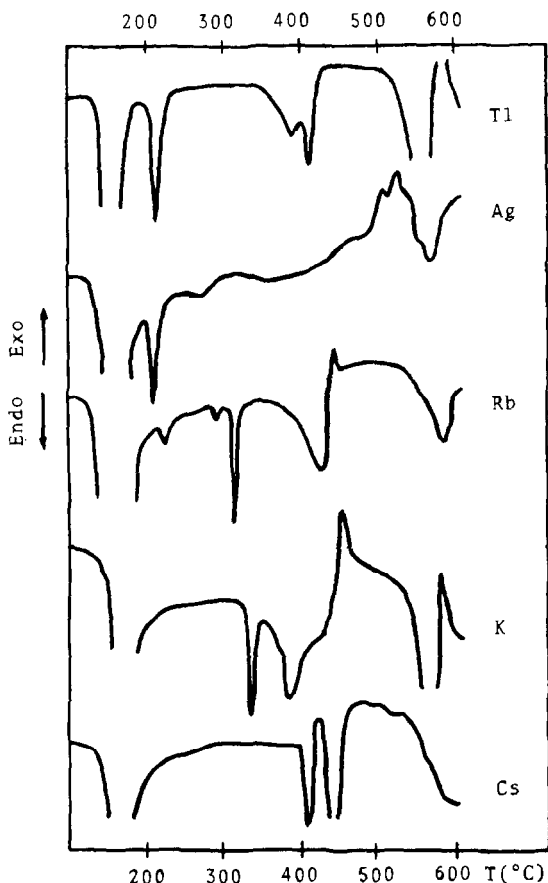
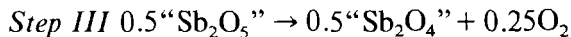
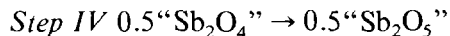


Fig. 2. DSC curves of the reactants $\text{Te}(\text{OH})_6$, Sb_2O_3 , MNO_3 ($\text{M} = \text{Tl}, \text{Ag}, \text{Rb}, \text{K}, \text{Cs}$).

later oxidation of the initial Sb(III) to Sb(V), that formally is represented above as a transformation of the trioxide to the antimony “pentoxide”.



In all cases an interesting process of partial reduction has been observed with the elimination of 0.25 mol O_2 per mole of formed product, at varied intervals of temperature. Formally one can table its relation with the well-known reduction of the pentoxide to antimony tetroxide, in which one half of the atoms would remain as Sb(V) and the other half as Sb(III).



Finally, there is a weight gain, equivalent to the previous elimination, which corresponds to reoxidation to Sb(V).

Table 1 shows the temperature intervals in which the stages of the above-mentioned reaction occur, and the corresponding variations in total weight, as well as the associated enthalpic effects.

TABLE 1

Temperature intervals (TI) weight loss (ΔP) and DSC enthalpic effects (EE), registered for the successive reaction steps

M	Step I			Step II			Step III			Step IV		
		TI(°C)	$\Delta P(\%)/EE$	TI(°C)	$\Delta P(\%)/EE$		TI(°C)	$\Delta P(\%)/EE$		TI(°C)	$\Delta P(\%)/EE$	
Ti	TG	50-230	5.6	230-430	14.3		550-610	15.6		610-700	14.4	
	DSC	130-190 200-225	endo endo (MP)	350-430	double endo		520-600	endo exo		-	-	-
Ag	TG	50-200	6.8	200-500	17.1		520-600	18.5		600-680	17.0	
	DSC	125-200 200-220	endo endo (MP)	no definite effects			490-550 550-600	exo endo		-	-	-
Rb	TG	50-230	7.1	230-590	17.6		600-635	18.9		635-750	17.5	
	DSC	130-220	endo	305-325 360-440	endo (MP) endo		540-600	endo		-	-	-
K	TG	50-210	7.5	210-500	17.5		500-590	21.1		600-740	19.2	
	DSC	125-220	endo	(overlapped with Step III)			540-600	endo exo		-	-	-
Cs	TG	50-200	6.5	200-560	16.3		600-650	17.8		700-720	16.2	
	DSC	120-220	endo	400-420 420-470	endo (MP) endo		550-600	endo		-	-	-

It can be seen that the first transformation (Step (I)) takes place at similar temperatures in all the cases, up to 200–230 °C, and is not altered by the presence of the other reactants. In the DSC curves we note an intense endothermic effect [18] and another endothermic one in the mixtures with nitrates of Tl (m.p. 205 °C) and Ag (m.p. 210 °C) attributed to fusion processes in both cases.

The next step (Step (II)) seems to be influenced by the melting point values of the metal nitrates, except in the case of the Tl, since more or less sharp variations are noticed in the gradients of the TG curves. This behaviour is attributed to the reaction of the nitrate which fuses with the other components in such a way that they produce simultaneously elimination of water and of the nitrogen oxides, as well as the oxidation of Sb(III) to Sb(V), probably due to the oxidizing character of said oxides. At temperatures above that of the m.p. of the nitrates, all the samples present a lumpy appearance and are amorphous to X-rays. In the sample of Tl the low m.p. of the nitrate does not appear to influence the reaction up to 300 °C.

In order to determine the transformations involved in this Step (II), we analysed the eliminated volatile substances by mass-spectrometry, finding H₂O and NO + NO₂, and their fragmentation products (chiefly 30 amu and 46 amu) at temperatures of 230–460 °C, in vacuum. On the other hand, comparing the thermal decomposition of telluric acid and that of the isolated metal nitrates, with that recorded in these mixtures, we observe that the progression of the dehydration is much greater in these experiments and also that the decomposition of the nitrates is now observed at considerably lower temperatures. These facts stress the interrelation existing between these two processes. The third significant occurrence in this Step (II) is the oxidation of all the Sb(III) incorporated in the mixed oxide formed to Sb(V) concomitant with the dehydration and the decomposition of the nitrate.

In fact, on carrying out this synthesis with Te(OH)₆, KNO₃ and Sb₂O₅ as initial reagents, the TG curve is analogous to that shown in Fig. 1 (sample K) up to about 350 °C and we observe a gradual weight loss up to 750 °C, without the bending near 440 °C, isolating the same solid phase of composition K(SbTe)O₆, characterized by X-ray diffraction.

This suggests that the formation of the pyrochlore is progressive and that all the Sb(V) is incorporated into the very stable structure of the mixed oxide, for which reason Steps (III) and (IV) are not observed. Moreover, this hypothesis is supported because the previous reactions, starting from Te(OH)₆, KNO₃ and Sb₂O₃ or Sb₂O₅, in the same conditions of thermal treatment but in a dynamic vacuum of some torr instead of in air, lead in the first case to a mixture of products where Sb₂O₄ is present and, in the second case, to the isolation of the potassium pyrochlore, as seems to be demonstrated by the X-ray diffraction pattern of the residues obtained at 750 °C.

The superimposed processes of Step (II) are shown in the DSC curves by the enthalpic effects shown in Table 1. In addition to the sharp peaks which

appear at the m.p. of nitrates, there are other endothermic effects, in general intense below 500 °C, as well as another exothermic in some cases, which seems attributable to the formation of the mixed oxide structure.

The interpretation of the DSC effects in Step (III) can be done in general terms, starting from the endothermic effect at temperatures close to 600 °C, which overlap with another exothermic in the samples of Tl and K. These facts are related to the weight losses equivalent to 0.25 mol of O₂ per mole of formed oxide and have been attributed to the reduction of half of the Sb(V) total to Sb(III), by analogy with the transformation of Sb₂O₃ at high temperature [19]. Effectively, although the samples show X-ray diffraction patterns with numerous lines of low intensity, some of them can be easily attributed to the antimony tetroxide [20]. This would confirm, therefore, the previous oxidation of all the antimony present to the Sb(V) state. This intermediate step in the oxidation of antimony to compounds of this type had not previously been reported [19].

Starting from the evaluation of the weight variation of Steps (III) and (IV) the composition M(SbTe)O₆ is reached in all cases for the final products at nearly 700–750 °C.

The X-ray diffraction patterns enable one to attribute confidently all the observed lines to a single-phase type pyrochlore (space group *Fd3m*, *Z* = 8) according to the assignment previously reported for some of them. Nevertheless, on subjecting these materials obtained to further thermal treatments at their formation temperature very clean-cut diffractograms are obtained, on the basis of which the reticular parameter has been calculated with greater

TABLE 2

Interplanar spacings (Å), relative intensities and Miller indices for Ag(SbTe)O₆

<i>h k l</i>	<i>d</i> _{calc}	<i>d</i> _{exp}	<i>I</i> / <i>I</i> ₀
1 1 1	5.905	5.906	8
3 1 1	3.084	3.078	22
2 2 2	2.953	2.954	100
4 0 0	2.557	2.561	32
5 1 1, 3 3 3	1.968	1.971	80
4 4 0	1.808	1.816	40
5 3 1	1.729	1.722	20
6 2 2	1.542	1.548	26
4 4 4	1.476	1.483	8
7 1 1, 5 5 1	1.432	1.431	8
6 6 2	1.173	1.173	10
8 4 0	1.144	1.144	8
9 4 4	1.044	1.044	6
9 5 1	0.989	0.989	10
8 8 0	0.904	0.903	8
10 6 2	0.864	0.834	35
8 8 4, 12 0 0	0.852	0.852	10

TABLE 3

Cell parameters (in Å) for $M(\text{SbTe})\text{O}_6$

Compound	a (Å)
$\text{Ag}(\text{SbTe})\text{O}_6$	10.2880
$\text{Tl}(\text{SbTe})\text{O}_6$	10.1207
$\text{K}(\text{SbTe})\text{O}_6$	10.1126
$\text{Rb}(\text{SbTe})\text{O}_6$	10.1486
$\text{Cs}(\text{SbTe})\text{O}_6$	10.1854

accuracy [16]. Table 2 shows the interplanar spacings, relative intensities and indexing for $\text{Ag}(\text{SbTe})\text{O}_6$, taken as an example. In Table 3 are collected the values of the a cell parameter of all the mixed oxides obtained by the powder method. All of them are of cubic symmetry and isostructural with the pyrochlore type [21].

Prior melting of the metal nitrates reduces the temperature necessary to obtain mixed oxides. The method of synthesis proposed in this study enables one to interpret the transformations recorded by the thermal analysis methods, and also the redox processes that particularly affect antimony. The comparative analysis of the influence of the change of metallic oxosalt (carbonates, oxalates, acetates, principally as non-oxidizing reagents) and of other oxoderivatives of Te and Sb on these same syntheses is in progress.

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