Synthesis and Characterization of the New Mixed Oxides $M(VTe)O_6$ (M = K, Rb, or Cs)

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New mixed oxides of the pyrochlore type of composition $M(VTe)O_6$ have been synthesized by reacting V_2O_5, $Te(OH)_6$, and MNO_3 (M = K, Rb, or Cs) (molar ratio 0.5:1:1) at 673 K. Characterization of these materials has been carried out by *X*-ray powder diffraction, giving cubic symmetry (space group $Fd\bar{3}m$) and lattice parameters a = 10.008(1) (M = K), 10.036(1) (M = Rb), and 10.483(1) Å (M = Cs). The atomic positions and *R* discrepancy factors were also calculated. Thermal analysis of the initial mixtures allowed the interpretation of the transformations involved up to decomposition of the pyrochlores. I.r. spectra are discussed on the basis of the structural type.

Mixed oxides of the pyrochlore structural type are well known and exhibit a great variety of potentially useful properties which include catalysis,[1] ferroelectricity,[2] ferromagnetism,[3] luminescence,[4] and ionic conductivity.[5] A review of the crystal chemistry and applications of oxide pyrochlores has been given recently by Subramanian *et al.*[6]

Compounds of the general formula $A_2B_2O_6O'$ constitute a family of oxides isotructural with the mineral pyrochlore, cubic, having space group $Fd\bar{3}m$, $Z = 8$, that is commonly described as a fluorite structure derivative;[7] alternative descriptions of the structure type have been reviewed elsewhere.[6] The structural formula for ideal pyrochlore is ${}^8A_2{}^6B_2{}^4O_6{}^4O'$, where A and B are metal cations, O and O′ are anions, and superscripts denote the co-ordination. Co-ordination of ions in the ideal case (complete anion sublattice) are $AO_6O'_2$, BO_6, OA_2B_2, and $O'A_4$. By removing combinations of A and O′ ions, a variety of defect structures ${}^6A_2{}^6B_2{}^4O_6$ and ${}^6A{}^6B_2{}^3O_6$ can be produced.[8]

The aim of the present paper is the preparation and physicochemical characterization of the cubic pyrochlores $M(V^VTe^{VI})O_6$ (M = K, Rb, or Cs) for the first time. These compounds could be related to $M(SbTe)O_6$[9] and to $M(NbTe)O_6$ and $M(TaTe)O_6$ whose structures have been discussed by Darriet *et al.*[10]

Experimental

The oxides $M(VTe)O_6$ (M = K, Rb, or Cs) were prepared from mixtures of analytical grade V_2O_5, $Te(OH)_6$, and MNO_3 in a V:M:Te molar ratio of 0.5:1:1 which were heated in air at 673 K for 24 h. (V_2O_5 was from Riedel de Haen, $RbNO_3$ from Aldrich, and the other reactants from Merck.) After thermal treatment the materials were quenched, weighed, and ground.

Thermal analyses were carried out in a Mettler TG50 thermobalance and in a Mettler DSC30 cell attached to a Mettler TA3000 controller. Samples were *ca.* 20 mg for thermal gravimetric analysis (t.g.) and *ca.* 5 mg for differential scanning calorimetry (d.s.c.). Thermal runs were performed at a heating rate of 5 °C min^{-1}.

Mass spectra were obtained by means of a thermogravimetric system built by coupling in a vacuum line a Sartorius 1410 microbalance with a Chesa furnace controlled by a microprocessor and a Leybold QF200 mass spectrometer.

Electron diffraction studies were performed by employing a high-resolution Siemens Elmiskop 102 electron microscope equipped with a goniometric grid. The working voltage was always 100 kV.

The i.r. absorption spectra were recorded with a Perkin-Elmer 1330 spectrometer using KBr pellets.

X-Ray powder diffraction data of the products were collected on a Siemens Kristalloflex powder diffractometer powered by a D500 generator and employing nickel-filtered Cu-K_α radiation (Tungsten was used as internal standard.) The unit-cell parameters were refined[11] from the 2θ values of the last seven reflections. The intensities were calculated with the LAZY-PULVERIX program[12,13] using scattering factors for neutral atoms, Lorentz and polarization factors, and a correction for anomalous dispersion. The arbitrarily chosen Debye–Waller factors for calculating the intensities were 0.30 and 0.80 $Å^2$ for Cs and O atoms, respectively. Values of 0.65 (V), 0.32 (Te), 0.70 (K), and 0.50 $Å^2$ (Rb) were obtained from those for Cs and O by interpolation of the corresponding atomic masses. The discrepancy factors between the observed and calculated intensities, $R = \Sigma(I_o^{\frac{1}{2}} - I_c^{\frac{1}{2}})/\Sigma I_o^{\frac{1}{2}}$, were computed after setting $\Sigma I_o = \Sigma I_c$ and taking into account all the reflections. The x value taken for each compound was that at the smallest R value.

Results and Discussion

The oxides $M(VTe)O_6$ were obtained as either beige (M = Cs) or greenish grey (M = K or Rb) powders, which gave good *X*-ray powder diffraction patterns. The samples were always obtained as single-phase cubic pyrochlores (space group $Fd\bar{3}m$, no. 227), and the presence of other phases was never detected. Electron microscopy showed that the compounds consist of crystals of homogeneous appearance. All the electron diffraction diagrams could be interpreted from the parameters obtained by *X*-ray powder diffraction, which seems to confirm that these compounds are single phases. The observed interplanar *d* spacings, their intensities, and the calculated values are showed in Table 1. The lowest discrepancy factors *R* were obtained for M in position 8*b* [origin of co-ordinates at centre ($\bar{3}m$)], V and Te randomly distributed in 16*c*, and the oxygen atoms in 48*f*.

Table 2 summarizes the relevant crystal data and the oxygen positional parameters, *x*. The observed interatomic distances were comparable with the sums of the corresponding radii.[14]

Figure 1 shows the t.g. and derivative thermogravimetric (d.t.g.) curves of the three initial mixtures of V_2O_5, $Te(OH)_6$, and MNO_3 (M = K, Rb, or Cs) in 0.5:1:1 molar ratios, carried out to 1 023 K. The d.s.c. curves of the same mixtures, recorded up to 873 K, the upper limit of the available technique, are shown in Figure 2. The melting points (m.p.) of the respective

Table 1. *X*-Ray powder diffraction data for the pyrochlores M(VTe)O_6 (M = K, Rb, or Cs)

	M = K			M = Rb			M = Cs		
hkl	d/Å	I_o	I_c	d/Å	I_o	I_c	d/Å	I_o	I_c
111	5.77	705	763	5.79	184	194	6.05	55	56
220	3.53	21	25	3.54	128	129	3.70	346	343
311	3.01	1 068	1 000	3.02	1 026	1 000	3.16	1 020	1 000
222	2.88	641	607	2.89	395	389	3.02	277	276
400	2.50	38	36	2.50	2	3	2.62	0	1
331	2.29	25	26	2.30	1	2	2.40	19	22
422	—	0	0	2.04	27	28	2.13	71	71
511; 333	1.926	288	278	1.931	292	289	2.017	327	329
440	1.769	428	430	1.774	400	394	1.853	311	310
531	1.692	104	108	1.696	19	21	1.772	0	2
620	1.582	26	25	1.586	51	53	1.657	116	117
533	1.526	122	123	1.530	123	124	1.598	150	152
622	1.509	234	226	1.513	145	145	1.580	150	107
444	1.444	21	29	1.448	2	6	1.513	3	4
551; 711	1.401	73	78	1.405	18	19	1.467	2	3
642	1.337	9	11	1.341	35	38	1.400	83	83
553; 731	1.303	192	195	1.306	201	205	1.364	210	210
800	1.2509	53	53	1.2545	46	50	1.3104	49	50
733	1.2226	1	2	1.2261	0	1	1.2807	1	3
660; 822	1.7940	8	10	1.1828	15	16	1.2354	39	41
751; 555	1.566	65	67	1.1589	76	79	1.2105	81	82
662	1.1479	89	86	1.1512	55	55	1.2025	39	40
840	1.1189	42	45	1.1221	10	11	1.1720	0	2
911; 753	1.0985	26	28	1.1016	2	4	1.1507	—	5
664	1.0668	6	8	1.0699	15	16	1.1175	31	31
931	1.0491	63	61	1.0521	61	63	1.0989	81	84
844	1.0214	90	87	1.0243	87	89	1.0699	71	75
771; 755; 933	1.0058	21	21	1.0087	2	3	1.0536	1	3
862; 10 20	0.9813	6	8	0.9841	20	24	1.0279	46	47
951; 773	0.9675	76	74	0.9702	81	80	1.0134	86	87
666; 10 22	0.9630	32	28	0.9657	20	21	1.0087	31	34

Table 2. Crystal data for the pyrochlores M(VTe)O_6 with estimated standard deviations in parentheses

M	a/Å	U/Å^3	D_c/Mg m^{-3}	x*	R
K	10.008(1)	1 002.1(1)	4.16	0.323	0.040
Rb	10.036(1)	1 010.8(1)	4.73	0.326	0.027
Cs	10.483(1)	1 152.0(1)	4.70	0.3014	0.026

* Origin at centre ($\bar{3}m$).

monovalent metal nitrates are labelled in order to appreciate their influence on the course of the reaction.[11]

The processes leading to the formation of the pyrochlores at temperatures up to 450 °C can be conventionally summarized by equation (1) (M = K, ΔW calc. 25.10, found 25.0%;

$$Te(OH)_6 + 0.5V_2O_5 + MNO_3 \longrightarrow M(VTe)O_6 + 3H_2O + 0.5N_2O_5 \quad (1)$$

M = Rb, ΔW calc. 22.64, found 22.3%; M = Cs, ΔW calc. 20.60, found 20.4%; ΔW = percentage weight loss).

Taking into account the evolution of the processes observed in the thermograms it is possible to differentiate two reaction steps, (2) and (3), in order to systematize the transformations.

$$0.5V_2O_5 + Te(OH)_6 + MNO_3 \xrightarrow[30-220\,°C]{-2H_2O} 0.5V_2O_5 + H_2TeO_4 + MNO_3 \quad (2)$$

$$\xrightarrow[220-450\,°C]{-H_2O-0.5N_2O_5} M(VTe)O_6 \quad (3)$$

Finally, at temperatures above 550 °C the decomposition process of the materials obtained can be written by equation (4)

$$M(VTe)O_6 \xrightarrow{-0.5O_2} MVTeO_5 \quad (4)$$

(M = K, ΔW calc. 3.71, found 3.8%; M = Rb, ΔW calc. 3.36, found 3.4%; M = Cs, ΔW calc. 3.05, found 3.2%).

The residues showed broadened *X*-ray powder diffraction peaks and it was not possible to confirm the formulation $MVTeO_5$ or to exclude the formation of several solid phases. It could be seen that the first transformation takes place at similar temperatures in all cases, up to 200—250 °C, and was not modified by the presence of other reactants. In the d.s.c. curves an intense endothermic effect appears between 100 and 200 °C attributed to the formation of $TeO_3{\cdot}H_2O$.[15]

The next step seemed to be influenced by the melting points of the metal nitrates, since more or less sharp variations were noticed in the gradients of the t.g. curves. This behaviour was attributed to reactions of the fused nitrates with the other compounds in such a way that they produce simultaneously the elimination of both water and nitrogen oxides. The complexity of the partial processes which take place in this step was registered in the d.t.g. curves. At temperatures above the melting points of the nitrates, all the samples showed a lumpy appearance and were amorphous to *X*-rays.

In order to determine the transformations involved in this step, mass spectrometric analysis of the volatile substances released was carried out. The presence of H_2O and NO + NO_2, and their fragmentation products (chiefly *m/e* 30 and 46) at

Table 3. I.r. spectroscopic data (cm^{-1}) for MB_2O_6 (M = K, Rb, or Cs; B = V or Te)

Compound	ν_1 ν(V=O)	ν_2 ν(B–O)	ν_3 ν(M–O)	ν_4 δ(O–B–O)	ν_5 δ(O–M–O) or [M–(BO_6)]	ν_6 δ(O–M–O)
K(VTe)O_6	950 (s)	695 (s)	660 (s)	460 (s)	410 (s)	345 (s)
Rb(VTe)O_6	950 (s)	690 (s)	645 (s)	470 (s)	405 (s)	330 (s)
Cs(VTe)O_6	945 (s)	680 (s)	635 (s)	480 (s)	400 (s)	320 (s)

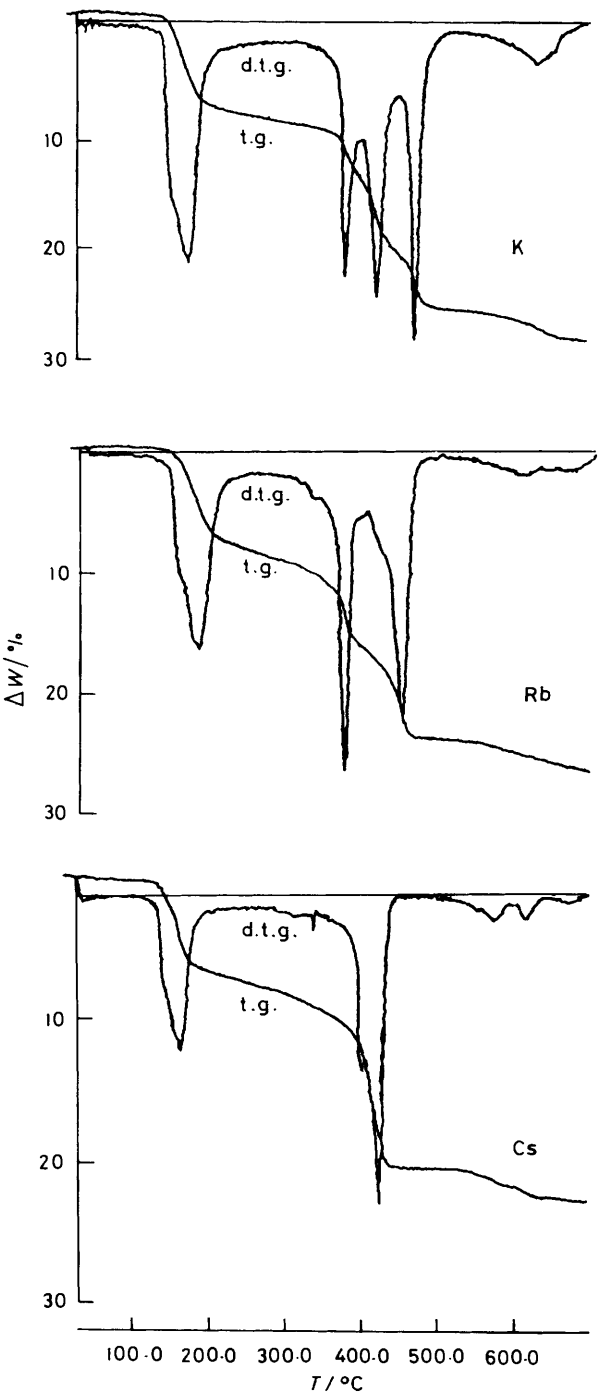

Figure 1. The t.g. and d.t.g. curves of the initial mixtures of V_2O_5, $Te(OH)_6$, and MNO_3 (M = K, Rb, or Cs)

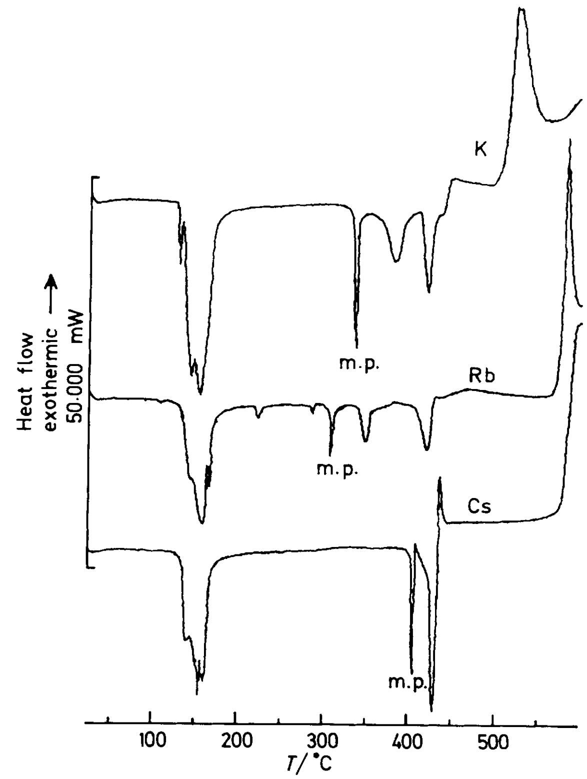

Figure 2. The d.s.c. curves of the initial mixtures of V_2O_5, $Te(OH)_6$, and MNO_3 (M = K, Rb, or Cs)

temperatures in the range 250—460 °C in a vacuum was detected. On the other hand, by comparing the thermal decompositions of orthotelluric acid and that of the isolated metal nitrates, with those recorded in these mixtures, a much greater progression of the dehydration processes and decomposition of the nitrates at considerably lower temperatures could be observed. The remaining thermal effects registered in the d.s.c. curves, below the melting points of the nitrates, corresponded to the well known phase transitions of these salts, and the last exothermic effect registered at 550 °C can be assigned to the final decomposition step, giving the substances formulated as $MVTeO_5$, partially crystallized.

Table 3 details the i.r. spectral data and the corresponding assignments, according to previous spectroscopic analysis for the pyrochlore-type compounds.[16–20] In addition, ν_1 could be attributed to ν(V=O) by analogy to V^V oxo-derivatives with pseudo-octahedral co-ordination.[21]

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