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Synthesis and Characterization of the New Mixed Oxides $M_2(GeTe)O_6$ (M = K, Rb, Cs)

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The mixed oxides $M_2(GeTe)O_6$ (M = K, Rb, Cs) were prepared by a solid-state reaction between $Te(OH)_6$, GeO_2, and MNO_3. In this paper their synthesis, X-ray powder diffraction patterns, IR spectra, and thermal behaviors are described. From the X-ray analyses, a cubic symmetry was established, resulting in the cell parameters $a = 9.917$ (M = K), 9.946 (M = Rb), and 10.012 Å (M = Cs). These materials have a pyrochlore-type structure, and the atomic positions and *R* discrepancy factors were also calculated.

Introduction

The compounds discussed in this paper seem to possess the pyrochlore structure. The space group is *Fd*3*m* (No. 227), and the unit cell contains eight structural units with the ideal formula $A_2B_2O_6O'$,[1,2] whereas in the defect pyrochlore structure anion and cation vacancies exist in the lattice to give the compositions $A_2B_2O_6O'_x$ ($A_2B_2O_{7-x}$; $0 < x < 1$) or AB_2O_6.[3-5] Since in all the cases the existence of different types of vacancies for diffusion of the A ions in the structure could be observed, these compounds can be regarded as potential ionic conductors.[6-8]

Until now several syntheses with this structural type have been described where a tetravalent metal or semimetal such as germanium is present. For example, cubic germanate pyrochlores ($A_2Ge_2O_7$; A = Gd, Lu, Y, Sc, In, Tl) were prepared by Shannon and Sleight[9] employing high-pressure techniques. Other studies developed by Bocquillon et al.[10] have shown that $Gd_2Ge_2O_7$, prepared at atmospheric pressure, has a tetragonal structure.[11]

At the present, there are not any references in the literature about mixed oxides of stoichiometry $A_2(GeM)O_6$ adopting a pyrochlore-type structure. On the other hand, the cell parameters for the derivatives $A^{3+}{}_2B^{4+}{}_2O_7$, where B = Si and Ge, are lower than 10 Å, probably due to the ionic radii of these elements in their usual oxidation state +4.[12]

This paper describes the preparation and identification by TG, IR, and powder X-ray diffraction techniques of the $M_2(GeTe)_6$ (M = K, Rb, Cs) compounds.

Experimental Section

The mixed oxides $M_2(GeTe)O_6$ were synthesized, in porcelain crucibles, by heating in air a mixture, in a 1:1:2 molar ratio, of $Te(OH)_6$, GeO_2, and MNO_3 (M = K, Rb, Cs) at 673 K for 36 h and later at 873 K for 24 h. The microcrystalline powders obtained are gray (K), dark gray (Rb), and black (Cs). The reagents (analytical grade) used in these experiments were supplied from Merck ($Te(OH)_6$, GeO_2, KNO_3, and $CsNO_3$) and Aldrich ($RbNO_3$).

These materials were characterized by chemical analysis using the standard methods.[13,14] The oxygen content was calculated by difference. The obtained results were in good agreement with the proposed formulas. Anal. Found (calcd) for K_2GeTeO_6: K, 20.7 (20.89); Ge, 19.0 (19.39); Te, 34.9 (34.08). Found (calcd) for Rb_2GeTeO_6: Rb, 36.3 (36.59); Ge, 15.1 (15.54); Te, 27.8 (27.32). Found (calcd) for Cs_2GeTeO_6: Cs, 46.8 (47.30); Ge, 12.7 (12.92); Te, 23.1 (22.70).

Thermogravimetric (TG) and differential thermogravimetric (DTG) curves were determined with a TG 50 microbalance attached to a Mettler TA 3000 analyzer, equipped with a TC 10 processor unit.

The IR absorption spectra were recorded with a Nicolet 60 SX spectrophotometer, and all the samples were compressed in KBr (4000–400 cm^{-1}) and polyethylene (400–140 cm^{-1}) pellets.

The *d* interplanar spacing measurements were made at room temperature in a Siemens Kristalloflex D-500 diffractometer, using Cu Kα radiation and employing W ($a = 3.16524$ Å) as internal standard. The unit-cell parameters were refined[15] from the 2θ values of the last nine reflections. X-ray diffraction intensities I'_o were collected by step scanning from 10 to 154° in 2θ with increments of 0.02° in 2θ and a counting time of 3 s each step, the goniometer being controlled by a DACO-MP V2 computer, which carried out the integration of the diffraction peaks and the background correction. As the graphite monochromator is not able to resolve Kα_1/Kα_2, intensities were integrated over the whole reflection peak (Kα_1 + Kα_2) even for the high-angle reflections in which both peaks were clearly not overlapped. The intensities were calculated with the program Lazy-Pulverix[16,17] using scattering factors for neutral atoms, Debye–Waller, Lorentz, and polarization factors, and correction for anomalous dispersion. The arbitrarily chosen Debye–Waller factors, Bj, for calculation of the intensities were 0.32 and 0.80 $Å^2$ for Cs and O atoms respectively. The values for K (0.71 Å) Ge (0.62 Å) Rb (0.51 Å) and Te (0.34 $Å^2$) were obtained from those of Cs and O by interpolation of the corresponding atomic masses. The discrepancy factors between observed and calculated intensities were computed from $R = \sum([I_o{}^{1/2} - I_c{}^{1/2}])/\sum I_o{}^{1/2}$, $I_o = KI'_o$, and $K = \sum I_c/\sum I'_o$ (I'_o = measured intensities, I_o = corrected measured intensities, and I_c = calculated intensities). Runs of the program were performed in a first approach with step increments of 0.01 for the values of *x* and *u* positional parameters and, later, with increments of 0.001. The *x* and *u* values (coordinates for M and O atoms, respectively) taken for each compound were those that gave the smallest *R* values.

Densities were determined by a pycnometric method (estimated error less than 0.2%) with CCl_4 as immersion liquid.

Results and Discussion

Chemical analysis results support the proposed stoichiometry $M_2(GeTe)O_6$ for all the phases (M = K, Rb, Cs). The crystallographic study of these materials was performed by means of X-ray powder diffraction patterns and *d* spacings, I_o and I_c values, assignments, and cell parameters are listed in Table I. From these results, the experimental interplanar spacings could be indexed as a face-centered cubic cell (*Fd*3*m*) with crystallographic pa-

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Table I. X-ray Diffraction Data for $M_2(GeTe)O_6$ (M = K, Rb, Cs)

	M = K			M = Rb			M = Cs		
hkl	d_{exp}, Å	I_o	I_c	d_{exp}, Å	I_o	I_c	d_{exp}, Å	I_o	I_c
111	5.73	747	760	5.47	235	200	5.78	82	80
220	3.51	21	20	3.52	116	100	3.54	238	200
311	2.99	969	1000	2.999	963	1000	3.019	975	1000
222	2.863	636	650	2.871	471	480	2.890	361	370
400	2.480	89	90	2.487	35	30	2.503	35	30
331	2.275	57	50	2.282	17	15	2.297	16	15
511	1.909	214	200	1.914	252	260	1.927	268	270
333									
440	1.753	274	275	1.758	314	320	1.770	271	275
531	1.676	111	100	1.681	50	50	1.692	50	50
533	1.512	76	75	1.517	89	91	1.527	96	95
622	1.495	167	170	1.499	150	150	1.509	94	90
444	1.431	31	30	1.436	19	20	1.445	15	14
551	1.389	63	60	1.393	35	35	1.402	27	20
711									
553	1.291	95	95	1.295	139	140	1.303	119	120
731									
800	1.240	36	31	1.243	41	40	1.252	27	20
751	1.145	32	30	...	...	5	...	...	5
555									
662	1.138	41	40	1.141	45	45	1.148	50	50
840	1.109	33	30	1.112	24	20	1.119	20	20
842	1.082	13	14	...	...	1	...	...	1
931	1.040	24	22	1.043	38	40	1.050	34	30
844	1.012	22	20	1.015	40	40	1.022	39	40

Table II. Crystallographic Results from X-ray Diffraction Data for $M_2(GeTe)O_6$

	M = K	M = Rb	M = Cs
a, Å	9.917 (1)	9.946 (1)	10.012 (1)
V, Å^3	975.39 (0)	983.98 (1)	1003.62 (0)
d_{calc}, Mg m^{-3}	4.457	5.044	5.573
d_{exp}, Mg m^{-3}	4.40	4.98	5.56
space group	*Fd*3*m*	*Fd*3*m*	*Fd*3*m*
Z	8	8	8
u(48f)[a]	0.424	0.426	0.433
x(32e)[a]	0.101	0.113	0.120
R	0.022	0.039	0.042

[a] *u* = coordinate for O atom; *x* = coordinate for M atom.

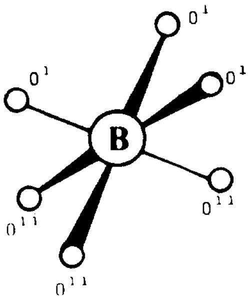

Figure 1. Coordination polyhedron around B (=Ge, Te) atoms.

rameters of about 9.9–10.0 Å (Table II). Peak intensities, when measured, and the systematic absences agree with a pyrochlore structure. None of the X-ray diffraction patterns showed superlattice reflections, and all the observed reflections were assigned according to the symmetry and cell parameters cited above.

The lowest discrepancy factors *R* were obtained for M = (K, Rb, Cs) in the 32(e) positions (origin at center 3*m*); Ge and Te are randomly distributed in 16(d) and oxygen atoms in 48(f). The observed interatomic distances are comparable with the sums of the radii of Shannon.[18] Figures 1 and 2 show the coordination polyhedra around the metal atoms (B and M) on the basis of the suggested structure, and the respective interatomic distances and angles are gathered in Tables III and IV.

B atoms (Ge or Te) are in a slightly distorted octahedral coordination, which becomes more regular when the radius of the

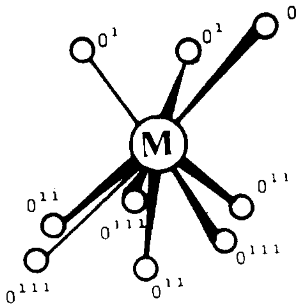

Figure 2. Coordination polyhedron around M (=K, Rb, Cs) atoms.

Table III. Interatomic Distances (in Å) and Angles (in deg), Calculated from the Experimental *u* Values, for the Coordination Polyhedra around B (=Ge, Te) Atoms

	M = K	M = Rb	M = Cs
	Distances		
B–O^{i}	1.91	1.91	1.89
B–O^{ii}	1.91	1.91	1.89
B–O (radii sums)	1.91	1.91	1.91
	Angles		
O^{i}–B–O^{i}	95.2	94.5	91.8
O^{i}–B–O^{ii}	180	180	180
O^{ii}–B–O^{ii}	84.8	85.5	88.2

Table IV. Interatomic Distances (in Å) and Angles (in deg), Calculated from the Experimental *x* and *u* Values, for the Coordination Polyhedra around M (=K, Rb, Cs) Atoms

	M = K	M = Rb	M = Cs
	Distances		
M–O^{i}	3.22	3.12	3.14
M–O^{ii}	2.75	2.88	3.03
M–O^{iii}	3.25	(3.41)	(3.53)
M–O (radii sums)	2.74	2.88	3.03
	Angles		
O^{i}–M–O^{i}	81.2	85.5	88.2
O^{i}–M–O^{ii}	88.9	89.7	90.0
	167	174	177
O^{i}–M–O^{iii}	83.1	...	...
	136		
O^{ii}–M–O^{ii}	99.5	94.7	91.9
O^{ii}–M–O^{iii}	49.9	...	...
	110		
O^{iii}–M–O^{iii}	80.3	...	...

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Table V. IR Spectroscopic Data (cm^{-1}) for $M_2B_2O_6$ (M = K, Rb, Cs; B = Ge, Te)[a]

	ν_1(B-O)	ν_3(M-O)	ν_4(O-B-O)	ν_5(O-M-O), ν_5(M-BO_6)	ν_6(O-M-O)
$K_2(GeTe)O_6$	745	620	460	420	345
$Rb_2(GeTe)O_6$	740	615	465	420	350
$Cs_2(GeTe)O_6$	720	580	470	415	355

[a] All absorptions shown are strong.

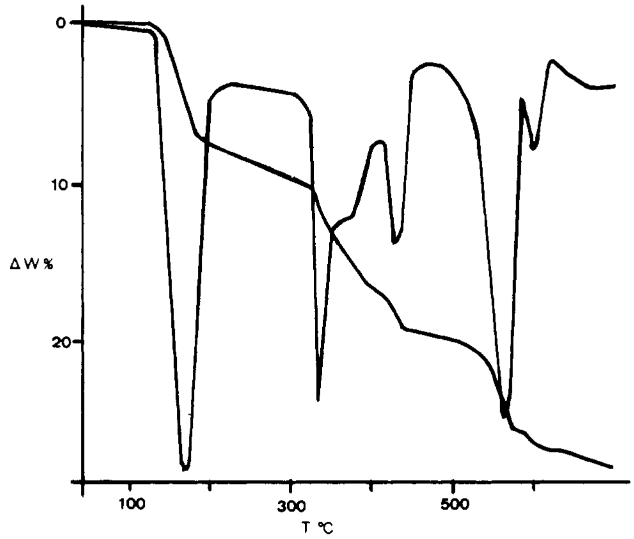

Figure 3. TG and DTG curves of the initial mixture leading to K(Ge-Te)O_6.

M cation is increased as suggested by the O-B-O angles. In all cases the observed B-O distances are in accord with those calculated from the sums of ionic radii. On the other hand, the coordination polyhedra around the alkali-metal cation (M) can be described as 3 + 3 + 3 for K (Figure 2); that is, there are three parallel planes of oxygen atoms, two of them (O^{i} and O^{ii}) being related to two opposite faces of a distorted-octahedral arrangement and the third set of oxygen atoms (O^{iii}) being located toward the middle of the edges O^{ii}-O^{ii} and at longer distances from K than the preceding ones. In Rb and Cs compounds these distances are considerably greater than the sums of respective ionic radii, and this fact suggests that coordination in these cases is reduced to 3 + 3 (O^{i} and O^{ii}). Again, the polyhedron around Cs is more regular.

In Table V are shown the IR absorption bands that are present in the range 745-345 cm^{-1} and their corresponding assignments, according to the previous spectroscopic analysis for the other pyroclore-type compounds.[19-23] As can be observed, the frequencies ν_1, ν_5, and ν_6 diminish, ν_4 increases with increasing atomic magnitude, and ν_3 becomes higher when the *a* cell parameter diminishes.

Figure 3 shows TG and DTG curves for the initial mixtures of $Te(OH)_6$, GeO_2, and KNO_3. When the alkali-metal reagents are $RbNO_3$ or $CsNO_3$, the behaviors of the thermal decomposition processes for these mixtures are closely similar. All the reactions can be associated with the loss of 3 H_2O per formula weight, two molecules being lost near 473 K and the third being progressively eliminated at higher temperatures overlapping with the melting process of metal nitrate (573 K for KNO_3). At this temperature a significant weight loss is observed, which was attributed to NO + NO_2 elimination from the reaction media[24] by several undefined steps. The process finished toward 923 K. The total weight loss measured is equivalent to 1 mol of dinitrogen pentoxide.

The successive transformations undergone by the initial mixtures during thermal analysis can be expressed as

$$Te(OH)_6 + GeO_2 + 2MNO_3 \xrightarrow{-3H_2O}$$
$$TeO_3 + GeO_2 + 2MNO_3 \xrightarrow{-NO,\ -NO_2} M_2(GeTe)O_6$$

which are similar to those of other related systems previously described by us.[25] On the other hand, the composition of the solid phases, isolated at the end of this reaction, seem to confirm the suggested stoichiometry.

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Registry No. $Te(OH)_6$, 7803-68-1; GeO_2, 1310-53-8; KNO_3, 7757-79-1; $RbNO_3$, 13126-12-0; $CsNO_3$, 7789-18-6; K_2GeTeO_6, 119696-12-7; Rb_2GeTeO_6, 119696-13-8; Cs_2GeTeO_6, 119696-14-9.

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