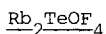


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PRELIMINARY NOTE

Synthesis and Structure of Dirubidium Oxotetrafluorotellurate (IV)



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SUMMARY

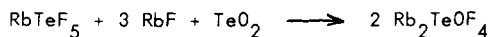
Dirubidium oxotetrafluorotellurate (IV) Rb₂TeOF₄ is described for the first time. This compound is isostructural with the two known oxotetrafluorotellurates M₂TeOF₄ (M = K, Cs). It crystallizes in the orthorhombic system with lattice constants a = 6,45 Å ; b = 14,18 Å ; c = 6,715 Å.

In a recent study [1] it has been clearly proved that vitrification of alkaline pentafluorotellurates (IV) MTeF₅ (M = K, Rb, Cs) is strictly governed by their partial reaction with oxygen.

The glassy material thus obtained contains an oxyfluoride M₂TeOF₄. The relative amount MTeF₅/M₂TeOF₄ depends on the conditions of the heat treatment and on the oxygen content of the gas surrounding the sample. To our knowledge the corresponding compound for M = Rb has not been described so far.

Synthesis of Rb_2TeOF_4 has been performed to allow a conclusive identification of the phases which appear upon crystallization of the glass.

The reaction described by Milne and Moffett [2] for K and Cs compounds was used :



RbF and TeO_2 are commercial reagents (Merck pur $\geq 99,8\%$). RbTeF_5 is obtained as described elsewhere [3],[4].

Manipulations, heat treatments and sampling were carried out in a glove-box under an atmosphere of dry and oxygen-free argon.

A mixture of powdered RbTeF_5 , RbF and TeO_2 with the above stoichiometric proportions was heated at 500°C for 1 hour. After cooling and grinding another treatment at 500°C was performed for 3 hours. Under these conditions Rb_2TeOF_4 was obtained quantitatively as a white solid.

The crystallographic study was performed with a Philips assembly (horizontal goniometer and 360 mm camera, copper source $1,5418 \text{ \AA}$). X-ray powder data are given in Table I.

TABLE I

X-ray powder diffraction data for Rb_2TeOF_4

| I/I ₀ | dobs. | dcalc. | h k l | I/I ₀ | dobs. | dcalc. | h k l |
|------------------|-------|--------|-------|------------------|--------|--------|-------|
| 10 | 4.86 | 4.875 | 0 2 1 | 10 | 2.227 | 2.229 | 0 6 1 |
| 5 | 4.41 | 4.420 | 1 1 1 | 20 | 1.947 | 1.945 | 2 4 2 |
| 10 | 3.78 | 3.810 | 1 3 0 | 10 | 1.906 | 1.906 | 2 6 0 |
| 5 | 3.53 | 3.545 | 0 4 0 | 20 | 1.880 | 1.879 | 3 3 1 |
| 20 | 3.37 | 3.360 | 0 0 2 | 5 | 1.836 | 1.834 | 2 6 1 |
| 100 | 3.31 | 3.315 | 1 3 1 | 5 | 1.792 | 1.796 | 3 1 2 |
| 25 | 3.21 | 3.225 | 2 0 0 | 5 | 1.714 | 1.714 | 0 8 1 |
| 5 | 2.528 | 2.520 | 1 3 2 | 5 | 1.695 | 1.695 | 1 5 3 |
| 15 | 2.362 | 2.363 | 0 6 0 | 10 | 1.664 | 1.660 | 3 5 1 |
| 30 | 2.335 | 2.326 | 2 0 2 | 5 | 1.6130 | 1.6125 | 4 0 0 |

The intensities were estimated visually. The observed reflexions were indexed using an a priori procedure. The cell dimensions were determined by a least-square analysis. Rb_2TeOF_4 is orthorhombic with $a = 6.45 \text{ \AA}$, $b = 14.18 \text{ \AA}$, $c = 6.715 \text{ \AA}$, $D_x = 4.22 \text{ g/cm}^3$, $Z = 4$.

This compound is isostructural with the two known M_2TeOF_4 ($M = K, Cs$) [2] having the M_2SbF_5 structure ($M = K, Rb, Cs, Tl$ [5] or NH_4 [5],[6]). Cell dimensions are given for comparison in Table II.

TABLE II

Orthorhombic cell dimensions (Å) for M_2TeOF_4 and M_2SbF_5 compounds

| M_2TeOF_4 | | | | M_2SbF_5 | | | |
|-------------|------|-------|-------|------------|-------|--------|-------|
| M | a | b | c | M | a | b | c |
| K (a) | 6.24 | 13.83 | 6.46 | K (c) | 6.244 | 13.67 | 6.491 |
| Rb (b) | 6.45 | 14.18 | 6.715 | Rb (c) | 6.399 | 13.88 | 6.745 |
| | | | | Tl(c) | 6.47 | 14.05 | 6.710 |
| | | | | NH_4 (c) | 6.489 | 14.09 | 6.710 |
| | | | | NH_4 (d) | 6.497 | 14.162 | 6.772 |
| Cs (a) | 6.65 | 14.53 | 7.04 | Cs^4 (c) | 6.652 | 14.45 | 7.099 |

(a) : ref. 2 - (b) : this work ; (c) : ref. 5 ; (d) : ref. 6

Moreover the indexing of the observed X-ray reflexions for Rb_2TeOF_4 (Table I) is compatible with the same space group $Cmcm$ (63) as for M_2SbF_5 compounds [5],[6].

The structure of these compounds contains isolated SbF_5E or $TeOF_4E$ anions whose geometry can be described by a slightly distorted octahedra in which the lone pair of electrons E located on an apical position plays a stereochemically active role.

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