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The Crystal Structure of Thallium Oxyfluoride, TlOF

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Thallium oxyfluoride, TlOF, crystallizes in the cubic system, space group $I\bar{4}3m$, with 32 formula units in a cell of $a=10{\cdot}78\pm0{\cdot}01$ Å. The intensities were collected by the Weissenberg method and the structure refined by the least-squares method to a conventional reliability index of 4·8% for 165 independent reflexions. The structure of TlOF is related to that of fluorite but with the Tl atoms in a distorted eightfold coordination.

Introduction

In recent years there has been a renewed interest in the structural and physical properties of simple oxyfluorides MOF (M = metal of the 3*d*, 4*d* and 5*d*, and rare-earth series). Several of these phases have been investigated in this laboratory.

A survey of the structural properties of the known MOF oxyfluorides indicates that they assume a variety of structures based on simple or complex derivatives of the fluorite and rutile structural models.

Several of the rare-earth oxyfluorides such as CeOF crystallize in the simple fluorite structure with oxygen and fluorine atoms randomly distributed on the fluorine sites (Zachariasen, 1954). Other rare-earth oxyfluorides crystallize in a rhombohedral distortion of the fluorite structure with an ordered arrangement of oxygen and fluorine (Mann & Bevan, 1970). The oxyfluorides TiOF, FeOF and VOF assume the rutile structure (Chamberland, Sleight & Cloud, 1970) while ScOF assumes the baddeleyite type (Holmberg, 1966).

The oxyfluoride of thallium was first reported by Gewecke (1909) with no further work being done until Grannec *et al.* (1970) were successful in preparing it by several methods. Sleight, Gillson & Chamberland (1970) also prepared TlOF and confirmed the results of Grannec.

A preliminary X-ray investigation indicated that TlOF crystallizes in a yet unknown structure with probably a CaF_2 sublattice. The work described here was undertaken in order to determine the structure of TlOF and further contribute to the understanding of the MOF chemistry.

Experimental

Single crystals of TlOF were prepared by the action of oxygen on TlF. Carefully dried oxygen reacts with very dry TlF under 5 kbar pressure and 500°C to give small and irregular-shaped crystals. The crystals appear black in colour indicating a small deviation from stoichiometry and the presence of Tl^+ ions. The highest value of x in the formula $TlO_{1-x}F$ was found to be 0·07 under the prevailing experimental conditions.

The powder diffraction data of TlOF were indexed on the basis of a cubic cell with $a=10{\cdot}78\pm0{\cdot}01$ Å. Single-crystal precession and Weissenberg photographs gave an identical value for the cell parameter. The measured density was $d_{\text{exp}}=9{\cdot}9\pm0{\cdot}1$ g.cm^{-3} indicating a cell containing 32 motifs. The calculated density is $d_{\text{calc}}=10{\cdot}14$ g.cm^{-3}. The reported error for the parameter represents the average deviation in the observed cell constant.

The Laue symmetry was found to be $m3m$. Systematic extinctions determined from zero and upper-layer Weissenberg and precession photographs occurred only for hkl: $h+k+l=2n+1$. These extinctions are consistent with space group $I432$, $I\bar{4}3m$ and $Im3m$. These results are also consistent with the observations of Sleight *et al.* (1970).

A single crystal of TlOF in the form of a small irregular sphere with an average radius of approximately 0·02 mm was chosen for data collection. This was mounted about its a axis and data were taken for $h=0$ to 10 using the multiple-film technique with an equi-inclination Weissenberg camera and Ni-filtered Cu radiation. A total of 740 reflexions were measured visually by comparison with a standard intensity scale. These data were scaled and averaged to give a total of 165 independent reflexions. Corrections were applied to the data for extended spot-shape and Lorentz-polarization effects. The inter-film and interlayer scaling was carried out by the usual scaling algorithm (Hamilton, Rollett & Sparks, 1965). An absorption correction was applied assuming that the crystal was spherical in shape. Since this correction was only approximate there may be an estimated error of 5% in the intensities of certain reflexions.

Structure determination and refinement

It was noted that certain obvious similarities exist between the powder patterns of TlOF and Tl_2O_3, the latter having a distorted fluorite structure with a quarter of the fluorine positions vacant. Therefore, it was decided that the structure of TlOF is probably a new type of distortion of the fluorite structure involving a doubling of its cell ($2a_{CaF_2}=10{\cdot}926$ Å). A three-dimensional Patterson function was calculated from which the positions of the heavy atom Tl were determined. The Tl–Tl vectors indicated that there are atoms at positions 0,0,0; $0,\frac{1}{2},\frac{1}{2}$; and *xxz* with $x=0{\cdot}26$ and $z=0{\cdot}04$. These positions are compatible only with space group $I\overline{4}3m$, a choice which was later confirmed by the successful refinement of the structure in this space group. Since there are 32 thallium atoms in the unit cell, 24 can be placed in position 24(*g*), (*xxz*); 6 can be placed at 6(*b*), $(0,\frac{1}{2},\frac{1}{2})$; and the remaining 2 at 2(*a*), (000). A structure factor calculation was carried out giving an *R* value:

$$R=\frac{\sum||F_o|-|F_c||}{\sum|F_o|}=0{\cdot}14$$

and confirming the placement of the Tl atoms. A Fourier synthesis revealed peaks most probably due to the oxygen and fluorine atoms, but no distinction was made between them. The 64 fluorines and oxygens were placed in position 8(*c*), (*xxx*) and 24(*g*), (*xxz*). Several cycles of isotropic refinement using the Tl atoms alone led to an *R* value of 0·105. When the fluorines and oxygens were included in the isotropic refinement the reliability value was lowered to 0·068. Finally, when a number of intense low-order reflexions affected by both absorption and extinction were excluded from the refinement, it settled to a final *R* value of 0·048. No anisotropic refinement was carried out. However, a refinement was tried with the oxygen and fluorine atoms in ordered positions with no significant difference being observed in the *R* value. Although no evidence was found indicating an ordered arrangement of oxygen and fluorine, this is not strictly conclusive since it would be difficult to distinguish between the two types of atoms in the presence of the very heavy thallium.

The refinement was accomplished using a full-matrix least-squares algorithm (Busing, Martin & Levy, 1962) modified to make real and imaginary anomalous dispersion corrections. The atomic scattering factors for oxygen, fluorine, and thallium were taken from *International Tables for X-ray Crystallography* (1962). The necessary parameters used for the anomalous dispersion were those given by Dauben & Templeton (1962). Unit weights were assigned to each reflexion.

The function $\sum w(|F_o|-|F_c|)^2$ was minimized, where F_o and F_c are the observed and calculated structure amplitudes and *w* is the weight. For the refinement procedure an overall scale factor was used.

The final positional and thermal parameters are given in Table 1. The final structure factors for observed reflexions are shown in Table 2. Those reflexions too weak to be observed had, at the end, calculated structure factors whose magnitude did not exceed the minimum observable value in neighbouring regions of reciprocal space.

Results and discussion

The structure deduced from the above refinement is shown in Fig. 1. As was predicted earlier from the comparison of the diffraction data of TlOF and Tl_2O_3, the structure of TlOF is indeed a rather distorted version of the fluorite structure. The calcium atoms are replaced here by thallium and the fluorine positions are occupied by either oxygen or fluorine. The thallium atom is situated in the centre of a distorted cube of oxygen and fluorine atoms. The basic arrangement of Tl in the TlOF unit cell is very much the same as that of Tl_2O_3 (Pauling & Shappell, 1930) and therefore explains the great similarity of their powder diffraction patterns (see Table 3). The very same arrangement of Tl is found in two other compounds possessing the distorted fluorite structure, $TiTe_3O_8$ and UTe_3O_9 (Galy & Meunier, 1971). These four compounds all have a CaF_2 cationic sublattice with $a/2=a_{CaF_2}$.

Table 1. *Final positional and thermal parameters for* TlOF

The standard deviations shown in parentheses here and in the text refer to the last decimal position of the respective values

	Position	*x*	*y*	*z*	$B(\text{Å}^2)$
Tl(1)	2(*a*)	0	0	0	0·34 (3)
Tl(2)	6(*b*)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0·31 (3)
Tl(3)	24(*g*)	0·2633 (1)	0·2633 (1)	0·0370 (1)	0·20 (3)
O,F(1)	8(*c*)	0·363 (4)	0·363 (4)	0·363 (4)	2·1 (5)
O,F(2)	24(*g*)	0·100 (3)	0·100 (3)	0·345 (4)	2·2 (5)
O,F(3)	8(*c*)	0·145 (5)	0·145 (5)	0·145 (5)	1·1 (5)
O,F(4)	24(*g*)	0·391 (5)	0·391 (3)	0·145 (5)	1·1 (5)

In the above phases a lowering in space group symmetry as compared with *Fm*3*m* of CaF_2 is noted, and also a doubling of the fluorite parameter.

The coordination polyhedra surrounding the Tl atoms vary in their of distortion depending on the kind of Tl atom involved (see Fig. 2). The atoms Tl(1) and

Table 2. *Observed and calculated structure factors for* TlOF

H	K	L	FO	FC	H	K	L	FU	FC	H	K	L	FO	FC
0	0	2	102	76	1	2	13	272	266	3	3	6	689	683
0	0	4	1586	1581	1	3	4	280	317	3	3	8	66	116
0	0	6	299	295	1	3	6	493	521	3	3	10	603	589
0	0	8	1091	1016	1	3	8	254	302	3	3	12	221	211
0	0	10	380	362	1	3	10	378	373	3	4	5	389	386
0	0	12	377	349	1	3	12	54	44	3	4	7	218	234
0	1	1	90	45	1	4	5	512	534	3	4	9	383	374
0	1	3	81	69	1	4	7	221	245	3	4	11	145	145
0	1	5	289	274	1	4	9	412	403	3	5	6	281	313
0	1	7	229	249	1	4	11	278	298	3	5	8	393	380
0	1	9	218	206	1	4	13	252	257	3	5	10	173	151
0	1	11	263	257	1	5	6	211	197	3	5	12	191	177
0	1	13	225	217	1	5	8	605	622	3	6	7	594	587
0	2	2	94	97	1	5	10	123	107	3	6	9	267	258
0	2	4	157	146	1	5	12	367	401	3	6	11	378	359
0	2	6	489	437	1	6	7	493	522	3	7	8	96	86
0	2	8	461	479	1	6	9	235	218	3	7	10	550	553
0	2	10	636	627	1	6	11	303	331	3	8	9	325	327
0	2	12	610	606	1	7	8	214	195	3	9	10	141	142
0	3	3	248	257	1	7	10	413	403	4	4	4	1110	1108
0	3	5	165	152	1	8	9	498	475	4	4	6	89	91
0	3	7	168	167	1	8	11	211	213	4	4	8	640	637
0	3	9	333	302	1	9	10	131	135	4	4	10	167	180
0	3	11	322	233	2	2	2	1973	1969	4	4	12	267	262
0	3	13	358	363	2	2	4	95	64	4	5	5	511	525
0	4	4	1592	1616	2	2	6	1280	1263	4	5	7	270	215
0	4	6	122	98	2	2	8	296	284	4	5	9	354	363
0	4	8	743	737	2	2	10	522	537	4	5	11	145	147
0	4	10	256	260	2	2	12	280	291	4	6	6	446	460
0	4	12	287	296	2	3	3	403	409	4	6	8	321	314
0	5	5	78	38	2	3	5	161	198	4	6	10	557	577
0	5	7	15	1	2	3	7	265	276	4	7	7	16	11
0	5	9	20	30	2	3	9	215	209	4	7	9	231	223
0	5	11	98	103	2	3	11	165	151	4	7	11	58	55
0	6	6	599	586	2	3	13	222	221	4	8	8	381	387
0	6	8	277	268	2	4	4	279	296	4	8	10	178	172
0	6	10	705	677	2	4	6	217	248	4	9	9	378	376
0	6	12	444	425	2	4	8	581	585	5	5	6	71	122
0	7	7	161	133	2	4	10	510	511	5	5	8	680	670
0	7	9	251	214	2	4	12	578	617	5	5	10	216	216
0	7	11	56	43	2	5	5	165	192	5	6	7	338	312
0	8	8	394	396	2	5	7	242	217	5	6	9	54	39
0	8	10	54	23	2	5	9	123	124	5	6	11	280	253
0	9	9	345	381	2	5	11	307	312	5	7	8	253	238
1	1	2	187	192	2	6	6	781	777	5	7	10	194	206
1	1	4	496	505	2	6	8	75	63	5	8	9	451	477
1	1	6	384	416	2	6	10	374	371	6	6	6	585	604
1	1	8	506	512	2	6	12	150	141	6	6	8	206	200
1	1	10	149	124	2	7	7	244	256	6	6	10	298	315
1	1	12	249	240	2	7	9	131	117	6	7	7	524	511
1	2	3	256	271	2	7	11	316	305	6	7	9	184	182
1	2	5	286	277	2	8	8	634	659	6	8	8	458	479
1	2	7	336	336	2	8	10	280	261	7	7	8	131	134
1	2	9	254	256	2	9	9	76	88	7	8	9	140	155
1	2	11	325	342	3	3	4	253	258	8	8	8	317	335

Table 3. *Crystallographic data of* Tl_2O_3, $TiTe_3O_8$, UTe_3O_9 *and* TlOF

Tl_2O_3	$TiTe_3O_8$	UTe_3O_9	TlOF
$Ia3$	$Ia3$	$Pa3$	$I\bar{4}3m$
a = 10·54 Å	a = 10·96 Å	a = 11·37 Å	a = 10·78 Å
8 Tl in 8(a)	8 Ti in 8(a)	4 U in 4(a)	2 Tl in 2(a)
24 Tl in 24(d)	24 Te in 24(d)	4 U in 4(b)	6 Tl in 6(b)
		24 Te in 24(d)	24 Tl in 24(g)

Tl(2) in positions 2(a) and 6(b) form much more regular polyhedra in comparison to Tl(3) in 24(g). The Tl(1) or Tl(2) cubes contain either eight longer bonds [2·52 (2) Å to 2·71 (2) Å] or eight shorter bonds [2·26 (2) Å to 2·28 (2) Å], all within the normal distribution of Tl–(O, F) bond lengths. On the contrary, the Tl(3) atoms form polyhedra (see Fig. 2) in which there are four short bonds [2·10 (2) Å to 2·27 (2) Å], three bonds of medium length [2·49 (2) Å to 2·69 (2) Å] and one longer bond [2·94 (2) Å]. This spatial arrangement of bonds around the Tl(3) atom seems to be very similar to that found in $TiTe_3O_8$ and UTe_3O_9 for the Te atom (Table 3). A further analogy is found in the case of ScOF (Holmberg, 1966) whose structure is a monoclinic distortion of the CaF_2 atomic arrangement, with Sc in a sevenfold coordination of 4 short bonds and 3 others at a slightly longer distance.

The large range of Tl–(O,F) bond distances observed here [2·10 (2) Å to 2·94 (2) Å], as well as in other thallium-containing compounds such as Rb_3TlF_6 (1·96 Å) (Bode & Voss, 1957) and $NaTlO_2$ (4·12 Å) (Hoppe & Werding, 1961) could be due to the significant polarizing effect of the thallium ion, as well as to covalency effects (Babel, 1967).

There exists in the structure of TlOF a network of Tl–Tl bonds, in the three dimensions, ranging from 3·445 (5) to 3·667 (5) Å, and comparable in length to the Tl–Tl distance observed in α-thallium (≃3·50 Å). This could explain the metallic conductivity observed by Grannec *et al.* (1970) in non-stoichiometric TlOF, which is possibly due to an overlap of the 6s orbitals of Tl, and which leads to a partially filled conduction band.

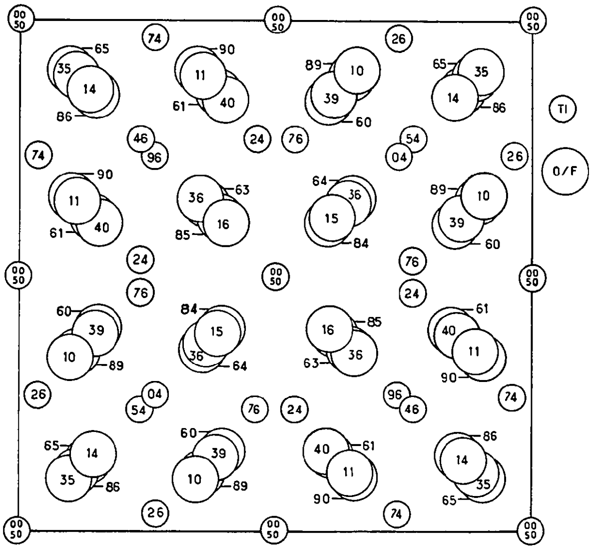

Fig. 1. Projection of the structure of TlOF on the (001) plane.

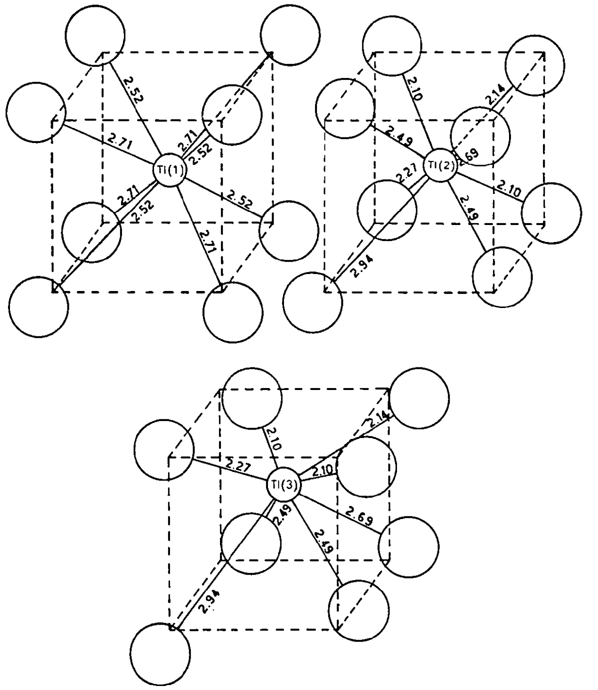

Fig. 2. Coordination polyhedra for several thallium atoms in the TlOF structure.

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