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CRYSTAL CHEMISTRY OF SOME TECHNETIUM-CONTAINING OXIDES

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Abstract—The crystal chemistry of technetium has been investigated in a series of simple binary and ternary oxide structures. An investigation of the system Tc—O under controlled conditions has revealed only one intermediate compound. Technetium-containing spinels can be synthesized in which technetium is on the octahedral sites. Technetium will enter the B-sites in ABO, compounds yielding perovskite, hexagonal BaTiO₂, and pyrochlore structures. Three rare-earth technetium pyrochlores with the formula Ln₂Tc₂O, have been prepared. The radius of the Tc⁴⁺ is shown to be 0.67 Å.

SINCE technetium has recently become available in larger quantities, it has been possible to study the chemistry of this element in some detail. Our interest in this element arises from the fact that it exists as a tetravalent element with unpaired 4d electrons, and may therefore be used to substitute in various ferrimagnetic structures in sixco-ordinated sites, and perhaps help elucidate structural details because of its large scattering power difference from the 3d elements.

A recent review on the chemistry of technetium⁽¹⁾ and a search through the recent Chemical Abstracts have revealed that an increasing amount of research in technetium chemistry is being carried out; however, the crystal chemistry of technetium in high temperature oxide systems has been generally neglected. From its position in the periodic table, one would expect technetium to behave similarly to manganese and rhenium. While there are many similarities between these three elements, in some respects their chemical behaviour is strikingly different as will be shown below.

GENERAL EXPERIMENTAL METHODS

1. Starting materials

As a source for technetium, NH₄TcO₄ was used. This product was obtained from the Oak Ridge National Laboratory, Tennessee. The other chemicals used were mostly of reagent grade purity.

2. Preparation of Tc and TcO,

For reactions with other metallic oxides, TcO, and Tc metal were prepared as follows:

- (1) TcO₃ was prepared by decomposing NH₄TcO₄ in a silica boat in a flow of pure N₂ gas $(pO_3 = 4 \times 10^{-6} \text{ atm})$ at 700°C to 750°C for 4–5 hr.
- (2) Tc metal was prepared by reducing TcO₃ in flowing H₃ gas at 700°C to 900°C for 4-5 hr.

3. Equipment

For all experiments in the temperature range up to 1000°C, a horizontal nichrome furnace was used. For experiments requiring temperatures in excess of 1000°C, a vertical platinum furnace was used. Chromel-Alumel thermocouples were used for temperature measurements up to 1000°C. At higher temperatures Pt/Pt-10Rh thermocouples were used. The temperature readings are accurate

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⁽¹⁾ R. COLTON and R. D. PEACOCK, Quart. Rev. 16, 299 (1962).

within $\pm 1-2^{\circ}$ C, but the reported measurements are estimated to be accurate to within $\pm 15^{\circ}$ C since no special care was taken to pinpoint equilibria, calibrate couples, etc.

All X-ray data were taken on a Norelco Diffractometer Unit. For lattice parameter measurements slow scan X-ray patterns were compared against an external NaCl standard. A few measurements of metal-technetium ratios were made on an ARL electron microprobe, since with this tool individual grains can be analysed.⁽⁸⁾ The probe analyses cited are perhaps only within ± 15 or 20 per cent accuracy. The lower than usual accuracy is due to:

(1) The inavailability of a well crystallized (above 1 μ crystal size) technetium standard,

(2) The necessity to use different wavelength radiation for technetium than for the other metal components, without appropriate absorption corrections.

The usual difficulties and precautions of work with radioactive species had to be observed, with the added complication in our case of the possibility of volatilizing the species.

THE SYSTEM TC-O

Only two oxides of technetium are well-characterized in the literature:⁽³⁾

- (1) The light-yellow Tc_2O_7 is said to melt at 119.5°C and boil at 310.6°C. It is formed easily by heating Tc or TcO_2 in dry oxygen at 400-600°C.
- (2) The black TcO₂ is thermally much more stable. It is slightly volatile at 900°C but does not decompose even up to 1100°C. According to MAGNELI,⁽⁴⁾ ZACHARIASEN has classified TcO₂ as belonging to the MoO₂ structure type, which has a distorted rutile structure.

Due to the low melting and boiling points of Tc_2O_7 , it was decided to restrict our experiments to the lower valence states. Attempts were made to prepare oxides intermediate in composition between Tc and TcO_2 as described below.

1. Studies of the system Tc-O2 under controlled atmospheres

In order to study the system $Tc-TcO_2$ under controlled oxygen pressures, gas mixtures of known oxygen contents were used: (1) an analysed nitrogen tank with a partial oxygen pressure of 4×10^{-6} atm, and (2) a CO-CO₂ mixture analysed at 0.75% CO, 99.25% CO₂.

In all cases the gas mixtures were passed over the sample for 4-5 hr at the temperatures indicated. The results of these experiments are summarized in Table 1.

Starting material	Gas mixture	Po,	Temp. (°C)	Phases found
NH TcO	Nitrogen	4×10^{-6}	330	R,S
NH TcO	Nitrogen	4 × 10-	460	R.S
NH TcO	Nitrogen	4 × 10-8	590	R,S
NH4TcO4	Nitrogen	4 × 10-*	700	R, faint trace of S
NH,TcO,	Nitrogen	4 × 10-6	750	R
NH TcO	Nitrogen	4 × 10-°	900	R
TcO ₁	0.75% CO, 99.25% CO,	4 × 10-11	600	M
TcO ₂	0.75% CO, 99.25% CO2	4·2 × 10-11	955	M

TABLE 1

 $R = distorted rutile structure (TcO_2)$

 $S = scheelite structure (TcO_3wN\cdot xO\cdot yH_2O\cdot zNH_3)$

M = hexagonal close-packed structure of technetium metal

(1) E. W. WHITE, Amer. Mineral, 49, 196 (1964).

⁽³⁾ S. TRIBALAT, Rhenium et Technetium, pp. 154-158. Gauthiers-Villars, Paris (1957).

(4) A. MAGNELI and G. ANDERSON, Acta Chem. Scand. 9, 1378 (1955).

 NH_4TcO_4 has a scheelite structure and it will be seen from the data that a scheelite-structure phase persists up to nearly 700°C in the runs carried out in nitrogen atmospheres with pO₃ near 10⁻⁶. The powder X-ray pattern of the scheelite-type phase is given in Table 2-A and shows that it is considerably smaller than the NH₄TcO₄

TABLE 2-A.—X-RAY POWDER PATTERNOF THE DECOMPOSITION PRODUCT OFNH4TCO4(Probably TCO3'WN'xO'yH3O'zNH3)Tetragonal $a_0 = 5.35$ Å, $c_0 = 11.91$ Å(Scheelite-type structure)d (Å)

a (A)	1/11	nkl	
4.89	57	101	
3.193	100	112	
2.978	. 6	004	
2.675	12	200	
2.344	12	211	
1.988	15	204	
1.890	6	220	
1.757	9	116	
1.626	9	312	
1.596	3	224	

parent. (NH₄TcO₄ has the unit cell dimensions of $a_0 = 5.790$ Å, co = 13.310 Å,⁽⁶⁾ compared to the intermediate decomposition product with $a_0 = 5.35$ Å, co = 11.91 Å). It appears likely that the phase is a defect scheelite which can possibly be represented as (NH₄)_{1-x} \Box_x TcO_{4-y} or N_{1-x} \Box_x T_cO_{4-y}.

When (a) high enough temperatures are used, or

- (b) sufficient time is allowed for the decomposition to take place, or
- (c) the grain size of NH_4TcO_4 is small enough so that the gases given off in

the decomposition are not readily captured by the empty lattice sites, TcO_2 is formed, and it does not revert to the scheelite type phase, even after standing in water at room temperature for a month.*

From Table 1 it can be seen that no intermediate technetium oxides could be formed with the available gas mixtures. It is unfortunate that even the most oxidizing CO-CO₂ mixture available could not reach the intermediate oxygen pressures of $10^{-6}-10^{-11}$ in the temperature ranges 500–950°C. Equilibrium studies above 950°C could not be carried out in this manner due to the appreciable volatility of TcO₂.

2. Studies in the system Tc-O₂ in closed systems

Since we could not prepare a new oxide of technetium (between Tc and TcO_2 in composition) under controlled partial oxygen pressures, attempts were made to prepare such a phase in a closed system.

* An analogous situation has been reported for the thermal decomposition of NH_4ReO_4 .⁽⁶⁾ The compounds NH_4ReO_4 and ReO_3 .² H_2O both belong to the scheelite structure. It is claimed that NH_4ReO_4 retains its structure even though the weight loss of the sample may be $\frac{1}{2}$ of that attained by complete decomposition to ReO_3 .

(8) B. J. MCDONALD and G. J. TYSON, Acta Cryst. 15, 87 (1962).

⁽⁶⁾ G. COEFFIER, K. TRAORE and F. BRENET, C.R. Acad. Sci. Paris 253, 103 (1961).

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Mixtures of Tc and TcO₂ were mixed in six different ratios, wrapped in platinum foil, vacuum-scaled into Vycor tubes, and then heated at about 970°C for 4½ days. Starting compositions are listed below with the corresponding results:

Starting composition	Products (X-ray)
TcO _{0.28}	TcO ₂ , Tc
TcO _{0.51}	TcO ₂ , new phase
TcO _{0.99}	TcO ₂ , new phase
TcO1.12	TcO ₂ , new phase
TcO1.20	TcO ₂ , new phase
TcO _{1.50}	TcO2

The distorted rutile structure of TcO_2 was noted in all patterns. In addition, one new phase was found in four of the six samples; the X-ray pattern (given in Table 2-B) can be indexed on the basis of a primitive pseudocubic unit cell with $a_0 = 9.45$ Å. It was found that in all these samples the technetium metal had partly reacted with the platinum foil forming a Pt-Tc alloy. This accounts for the absence of all but TcO₂ peaks in the TcO_{1.80} sample.

TAB	LB	2-B X-RA	Y PO	WDER	PATTER	N	OF	
THE	IN	TERMEDIATE	Tc-O	PSEUD	OCUBIC	PH	ASE	
		0.	~ 0.4	IS Å				

d (Å)	<i>I</i> / <i>I</i> ₁	hkl
6.69	100	110
4.23	3	210
2.987m	13	310
2.620	5	320
2.226	9	330, 411
1.919	2-25	
1.889	6	430, 500
1.857	2	510, 431
1.759	2)	520
1.749	21	520
1.669	13	440
1.336	1	710, 550, 543

The same new pseudocubic phase was obtained in another experiment: a mixture of Tc and TcO₂ corresponding to the composition $TcO_{0.10}$ was put into a small silica tube which was placed into a large tube. The larger tube was sealed and then heated slowly up to 1250°C over a period of 12 hr. Then the sample was kept at 1250°C for another 12 hr. When the sample was quenched, it was found that part of the sample had remained in the small tube and part of it had volatilized into the cooler parts of the large tube.

X-ray analysis showed that the sample which had remained in the small tube consisted almost exclusively of technetium metal with only a trace of TcO₂. The volatilized part of the sample consisted of Tc metal, TcO₂ and the pseudocubic intermediate phase mentioned above. The TcO₂ phase in the volatilized sample had many strong peaks missing, possibly due to preferred orientation. Microscopic

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examination showed many very fine whiskers emanating from the bulk of the sample.

The pseudocubic phase can be assumed to be of a composition intermediate between Tc and TcO_2 , since it has been formed only in the presence of both components; however, the stoichiometry and structure of this phase are still unknown.*

3. The TcO₂ phase

The X-ray pattern of TcO₂ is given in Table 2-C. This phase was prepared by the thermal decomposition of NH₄TcO₄ at 950°C in a flow of nitrogen for 4-5 hr. The pattern of this phase is very similar to but not identical with that given by COBBLE.⁽⁷⁾ Both patterns appear to belong to a distorted rutile structure; however, neither of these patterns fits closely ZACHARIASEN's⁽⁴⁾ approximate cell dimensions for TcO₂ (MoO₂ structure with $a_0 = 5.53$ Å, $b_0 = 4.79$ Å, $c_0 = 5.53$ Å, and $\beta = 120^\circ$.)

d (Å)	<i>I</i> / <i>I</i> ₁	
3.355	100	6.94
2.448	40	
2.428	14	
2.386	8	
2.357	8	
2.179	2	Sele
2.164	2	1
1.865	1	21
1.805	1	
1.732	<1	
1.708	12	
1.703	21 /	
1.689	11	
1.675	18	
1.544	2	
1.506	4	1213 9
1.492	4	
1.424	2	10 4
1.388	5	
1.380	2	
1.369	2	
1.313	3	
1.307	3	
1.222	<1	
1.193	3	
1.188	2	
1.117	2	
1·307 1·222 1·193 1·188 1·117	3 <1 3 2 2	

TABLE 2-C.-X-RAY POWDER PATTERN OF TCO₂ (Possibly monoclinic MoO₂ structure)

4. The oxygen-rich Tc metal phase

There is some evidence that technetium metal can hold small amounts of oxygen in its lattice. When NH_4TcO_4 is thermally decomposed in a flow of hydrogen at very

• One unindexable peak of the pseudocubic phase varies greatly in intensity and may therefore belong to still another phase.

⁽¹⁾ J. W. COBBLE, Ph.D. Dissertation, University of Tennessee (1952).

low temperatures, $(230-300^{\circ}C)$, a very poorly crystallized Tc metal phase results. This phase has very broad and poor X-ray peaks with comparatively high *d*-values (*d*101 values are as high as 2.100 Å). The metallic phases obtained by reducing TcO₂ with the 0.75% CO-99.25% CO₂ mixture (see Table 1) are somewhat better crystallized with slightly smaller *d*-values. Still smaller *d*-values are obtained for the metal phase which is obtained when TcO₂ is gradually reduced by a stream of H₂ gas between 300 and 700°C over a period of several hours and the resulting phase is heated in H₂ gas for 2½ days at 920°C. The X-ray pattern of this phase, given in Table 2-D, is very sharp, indicating that the Tc metal phase is relatively well crystallized.

TABLE 2-D .- X-RAY PATTERN OF TC METAL

d (Å)) 1/11	hkl	1
2.373	26	100	115
2.199	26	002	
2.089	100	101	
1.613	16	102	
1.371	21	110	84.5
1.247	6 23	103	1.2
1.187	0 3	200	
1.163	4 22	112	
1.146	2 16	201	
1.099	8 3	004	
1.044	7 4	202	
0.998	1 3	104	
0.922	8 10	203	
0.897	3 2	210	
0.879	3 19	211	
0.857	9 13	114	
0.830	9 7	212	5.1
0.825	0 10	105	

While our unit cell dimensions for the maximum reduced metallic technetium $(a_0 = 2.741_8, c_0 = 4.400 \text{ Å})$ are in good agreement with the corresponding values given by LAM et al.⁽⁸⁾ $(a_0 = 2.743 \text{ Å}, c_0 = 4.400 \text{ Å})$, MOONEY's cell dimensions⁽⁹⁾ for technetium are considerably smaller $(a_0 = 2.735 \text{ Å}, c_0 = 4.388 \text{ Å})$. It is possible

that MOONEY's unit cell represents a virtually oxygen-free technetium, while the metal phases obtained in our investigations still contain appreciable amounts of oxygen. On the other hand, MOONEY's lower cell dimensions may indicate an impure technetium sample.

In a recent article by PICKLESIMER and SEKULA⁽¹⁰⁾ it is pointed out that the abnormally large superconducting transition temperatures of Tc reported in the earlier literature were probably due to dissolved oxygen in the metal. The same investigators also reported that the powder particles of Tc are porous and spongy. This same sponginess was also noted in our technetium samples. PICKLESIMER and

⁽⁰⁾ D. J. LAM, J. B. DARBY, JR., J. W. DOWNEY and L. J. NORTON, Nature, Lond. 192, 744 (1961). ⁽¹⁾ R. C. L. MOONEY, Acta Cryst. 1, 161 (1948).

(10) M. K. PICKLESIMER and S. T. SEKULA, Phys. Rev. Letters 9, 254 (1962).

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SEKULA attribute the sponginess to dissolved and/or entrapped and unreduced oxide existing as a centre between two surface layers of reduced metal. We have cited evidence above for the existence of crystalline solution of oxygen in Tc, and have not found any X-ray evidence for oxide layers between the metallic Tc; if such oxide layers exist, they must be amorphous. The lowest temperature maximum oxygen phases should be studied for their superconducting transition temperatures.

SOME BINARY AND TERNARY OXIDES OF TECHNETIUM

1. Preparation of samples and experimental procedure

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Due to the high volatility of TcO_2 , all the experiments were carried out in sealed platinum capsules in place of evacuated silica tubing. A few preliminary experiments with silica or Vycor tubing showed that TcO_2 (sometimes partly reacted with the other oxide phase) volatilized and condensed in the colder parts of the tube to an appreciable extent. Also, the use of Vycor tubing sometimes resulted in the formation of technetium containing silicates, such as Ba-Tc and Sr-Tc silicates. In all these cases, the products were highly heterogeneous.

In all cases listed below, the samples were prepared and reacted as follows: carefully weighed out quantities of TcO_2 were mixed with the proper amounts of the other metallic oxides (MnO, SrO, Sm_2O_3 , etc.) in a small partly folded platinum foil. The foils containing these small (15–100 mg) samples were then folded up tightly, inserted into platinum capsules and sealed. The capsules were then preheated $200_{\tau}400^{\circ}C$ below the final heating temperature for a day or so. Then the final heat treatment took place at the temperatures and for the durations indicated in the tables below. The samples were then water quenched, opened and examined by X-ray diffraction.

In over half of the cases reported below, the desired phases could be prepared in a virtually pure state, judging from the X-ray data. In the remaining cases, small amounts of impurities were picked up in the X-ray powder patterns. These impurities usually consisted of the non-volatile starting materials. In all cases where small amounts of impurities were found the compound concerned is labelled with an asterisk (*). Such compounds may be slightly off the indicated stoicheiometry.

Firing temperatures were generally kept below 1250°C, since above that temperature leaks frequently develop in the platinum capsule. Even below that temperature, leaks sometimes occurred, usually resulting in the complete loss of TcO_2 from the capsule.

2. Technetium containing spinels

It was particularly interesting to attempt the synthesis of technetium-containing spinels since there is the possibility of finding new ferrimagnetic compounds. Tc^{4+} has a d^3 electron configuration and, from a simple energy level consideration, has a strong octahedral site preference of about 9 Dq (oct.). One would expect, therefore, to be able to prepare A_2TcO_4 spinels in which the second ion has no strong preference for either tetrahedral or octahedral sites.

Table 3 presents some data on successfully attempted technetium spinels with other divalent oxides. In all cases, the spinel phases were black, opaque and well crystallized (crystals of up to 50 μ were visible under the microscope).

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Approximate composition of spinel	Final temp. of heat treatment (°C)	Duration of heat treatment	Unit cell edge a° (Å) ± 0.003 Å	Ferrimagnetic (liquid nitrogen temps)
Mg ₁ TcO ₄	1185	1± days	8.498	No
*Co,TcO,	1210	2 days	8.450	No
Mn ₂ TcO ₄	1215	2 days	8.682	Yes
CoMnTcO4	1210	2 days	8.563	No
*CoNiTcO.	1125	1 days	8-449	No
NiMnTcO.	1215	1 day	8.551	Yes
NiZnTcO.	1185	1 days	8.462	No
*NiCdTcO.	1125	11 days	8.786	No

The qualitative presence of ferrimagnetism was determined by immersing a small vial containing the spinel in liquid nitrogen for about 2 mins. The sample was then withdrawn quickly and tested with a small magnet. Quantitative measurements on the susceptibilities of these phases as a function of temperature are now in progress.

An infra-red absorption pattern was taken for Mg₂TcO₄. The pattern showed two broad bands centred at about 15.8 and 21.6 μ , which is typical for a spinel. An electron microprobe examination of Mg₂TcO₄ gave a Mg/Tc ratio of 1.91.

Table 4 compares the unit cell dimensions of some technetium spinels with their titanium analogues. It is seen that in all four cases, the Ti spinels have smaller unit cells.

I ABLE 4				
Type of spinel	Cell dimensions (Å)	References		
Mn ₁ TcO ₄	8.682			
Mn _a TiO ₄	8.67	11		
NiZnTcO4	8.462	1 - C.		
NiZnTiO4	8.41	12 (p. 76)		
Mg ₂ TcO ₄	8.498	-		
Mg TiO4	8.445	12 (p. 49)		
Co,TcO,	8.450	-		
Co,TiO,	8.43	11		

Other technetium-spinels were attempted unsuccessfully. Among them were: Cu_2TcO_4 , Ni_2TcO_4 , $NiTc_2O_4$, $FeTc_2O_4$, Fc_2TcO_4 and Zn_2TcO_4 . In the case of the attempted Cu_2TcO_4 spinel, an apparently homogeneous phase was obtained; however, the X-ray pattern was quite complex and was not indexed. In many of the other cases, leaks developed, resulting in the loss of TcO_2 . In the case of the two attempted Fe spinels and for the attempted $NiTc_2O_4$, metallic Tc was mixed with TcO_2 and Fe_2O_3 or NiO in a small silica tube, which was then inserted into the platinum capsule and sealed.

Typical of these unsuccessful attempts were our investigations with the $Fe_{2}TcO_{4}$ composition. At high temperatures (above 1200°C) and long reaction times, the platinum capsule develops a leak while at low temperatures, or short reaction times

⁽¹¹⁾ HOLGERSSON and HERRLIN, Z. Anorg. Chem. 198, 78 (1931).
⁽¹³⁾ R. DATTA, Ph.D. Thesis, Pennsylvania State University (1961).

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(a few hours) at higher temperatures, a partial reaction takes place only, yielding a ferrimagnetic technetium-rich Fe_3O_4 and an iron-rich TcO_2 .

In all of the successfully prepared technetium spinels, the technetium is most probably in the +4 state and probably occupies predominantly octahedral sites. The unsuccessful attempts to prepare $Ni_{2}TcO_{4}$ and the successfully attempted $NiZnTcO_{4}$ can be explained in terms of the low preference of Tc^{4+} for tetrahedral sites in spinels. Ni^{2+} has a strong octahedral preference while Zn^{2+} tends to orient tetrahedrally in spinels. Thus the crystal field stabilization energies are ideal for spinel formation in the case of $(Zn^{2+})^{1V}$ (NiTc)^{VI}O₄ but decidedly adverse for the formation of the two end members.

3. TiO₂-TcO₂ crystalline solutions

When a distorted rutile structure is made to react with TiO₂, an undistorted rutile structure usually results over a large composition range. Such were the findings of MARINDER and MAGNELI.⁽¹³⁾ Technetium oxide is no exception to the rule. An undistorted rutile structure with $a_0 = 4.636$ Å and $c_0 = 2.974$ Å is obtained for the composition Ti_{0.6}Tc_{0.4}O₂ (determined by electron probe) when the appropriate TiO₂ (anatase)-TcO₂ mixture is heated in sealed platinum capsules at 1210°C for one day. The cell dimensions are appreciably larger than those for pure TiO₂ given in the ASTM file as $a_0 = 4.594$ Å, $c_0 = 2.958$ Å.

This close resemblance in behaviour between Ti^{4+} and Tc^{4+} suggests that technetium would make a good radioactive tracer with which to follow the reactions of titanium in titanate ceramics.

4. Some ATcO₃ structures

Table 5 summarizes the results of our investigation of the structures of some technetium-containing ABO₈ compounds.

ABO ₃ phase	Reaction temp. (°C)	Duration of final heat treatment	Mc/Tc ratio by electron microprobe	Resulting ABO ₃ structure (X-ray evidence)
SrTcO ₈	1225	1–3 days	1.15	Very slightly distorted perovskite structure with $a_0 = 3.95$ Å
BaTcO ₈	1030-1225	1 day to 1 week	1.04	Hexagonal BaTiO ₃ structure with $a_0 = 5.758$ Å, $c_0 = 14.046$ Å
PbTcO ₃	890	3½ days	0.95	Pyrochlore structure $a_0 = 10.361$ Å

TABLE 5

The distortion in the $SrTcO_3$ perovskite is so slight that the majority of peaks cannot be well separated from each other in a slow-scan X-ray pattern even at high 2θ values. Most of the peak clusters are doublets, triplets or quadruplets, which suggests that the distortion is of an orthorhombic or lower symmetry. An electron

(18) BENGT-OLOV MARINDER and A. MAGNELI, Acta Chem. Scand. 12, 1345 (1958).

probe scan of a small sample revealed that $SrTcO_3$ has a cube-like habit with crystals up to 40 μ in size.

The X-ray pattern for BaTcO₃* bears a very close resemblance to that of hexagonal BaTiO₃ given by RASE and ROY⁽¹⁴⁾. The unit cell volume of BaTcO₃ is slightly larger than that for hexagonal BaTiO₃ ($a_0 = 5.735$ Å and $c_0 = 14.05$ Å according to BURBANK and EVANS⁽¹⁵⁾) BaTcO₃ crystallizes in hexagonal platelets (up to 15 μ in size) as was revealed by an examination with the electron microprobe.

Although the pyrochlore structure is commonly considered to be an $A_2B_2X_7$ structure, pyrochlores with compositions near AB_2X_7 or $A_{1+x}B_2O_{6+x}$ ^(16,17) are also known. This is possible because one of the seven oxygens and all of the large cations (A sites) are not really necessary for the stability of the structure.⁽¹⁶⁾ Thus our finding that the lead-technetium mixture gave a pyrochlore phase is not surprising. Its final composition seems to be close to the ABO₃ stoicheiometry since PbO and TcO₂ were used in equimolar ratios and no unreacted PbO (or any other impurity phase) was detected in the X-ray pattern. Pyrochlores with an ABO₃ stoicheiometry are not so well known, but some have nevertheless been reported in the literature. For instance, SCHREWELIUS⁽¹⁸⁾ has reported pyrochlores of compositions NaSbO₃ and AgSbO₃.

5. Rare earth-technetium pyrochlores and the ionic radius of Tc4+

Our experiments with rare earth-technetium mixtures of the pyrochlore stoicheiometry are summarized in Table 6.

TABLE 6					
Composition of pyrochlore	Final heat treatment (°C.)	Duration of heat treatment	Unit cell edge a_0 (Å) ± 0.004 Å		
SmaTcaO,	1200-1230	3 days	10.352		
*Dy Tc O,	1200-1230	3 days	10.246		
*EraTcaO7	1200-1230	3 days	10-194		

Of the pyrochlore peaks with odd hkl, only the (331) and the (511) peaks were observed. This is to be expected for pyrochlores where the two cations do not differ greatly in scattering power.

As has already been shown by MONTMORY and BERTAUT⁽¹⁹⁾, the rare earth pyrochlores are sensitive indicators of the relative sizes of both the tetravalent ions and the trivalent rare earth ions. This is demonstrated again in Fig. 1 below, where the unit cell edges of four series of rare earth pyrochlores are plotted against the atomic number of the rare earths. The Goldschmidt radii for Ti⁴⁺, Ru⁴⁺ and Ir⁴⁺

* Indexed X-ray powder data for the known structures of Mg₉TcO₄, BaTcO₅ and PbTcO₅ have been submitted to the ASTM X-ray powder data file.

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Crystal chemistry of some technetium-containing oxides



FIG. 1.—Unit cell edges of some rare earth pyrochlore structures are plotted against the atomic number of the rare earths. The rare earth-technetium pyrochlores were prepared in this study. The literature sources of the other data are as follows:

> $(RE)_{a}$ Ir₂O₇—Reference (19) (RE)₂ Ru₂O₇—Reference (20) (RE)₄ Ti₂O₇—Reference (21).

are 0.64 Å, 0.65 Å and 0.66 Å respectively. Since the four straight lines in Fig. 1 are parallel and about equally spaced with respect to each other, it appears that an ionic radius of 0.67 Å can be assigned to Tc^{4+} .

The corresponding cell dimensions for the rare earth zirconate⁽²¹⁾ and the rare earth stannate pyrochlores^(21,22) are larger than those reported above, but not as large as one might expect from their Goldschmidt radii. This is especially true for the zirconate pyrochlores.

SASVARI⁽²³⁾ reports a radius of 0.70 Å for Tc⁴⁺. However, this value appears to be based on erroneous data: a monoclinic unit cell for TcO₂ of $a_0 = 5.53$ Å, $b_0 = 4.79$ Å, $c_0 = 5.93$ Å, $\beta = 120^{\circ}$. ZACHARIASEN'S unit cell (according to MAGNELI and ANDERSON⁽⁴⁾) has $c_0 = 5.53$ Å. Apparently SASVARI made an error in copying ZACHARIASEN'S unit cell from MAGNELI and ANDERSON'S article.

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ATTEMPTED RHENIUM ANALOGUES OF SOME TECHNETIUM PYROCHLORES AND SPINELS

An attempt was made to prepare rhenium pyrochlores of the type $Sm_2Re_2O_7$, $Dy_2Re_2O_7$ and $Er_2Re_2O_7$ under conditions similar to those used to prepare the technetium compounds. In none of the three cases was a pyrochlore phase obtained. X-ray and microscopic observations show that $Dy_2Re_2O_7$ and $Er_2Re_2O_7$ are homogeneous well crystallized phases. Judging from their complex and as yet unindexed X-ray patterns, $Dy_2Re_2O_7$ and $Er_2Re_2O_7$ are probably isostructural. In the case of the attempted samarium pyrochlore, two phases were observed under the microscope.

Attempts to prepare spinels of the type Mg_2ReO_4 , Mn_2ReO_4 and $MnNiReO_4$ have similarly failed. In all three cases, the products consist of at least two phases: (1) the monovalent oxides (MgO, MnO and MnO-NiO solid solution) and (2) a rheniumrich phase with a highly complex X-ray pattern.

It is most interesting to note that Re^{4+} and Tc^{4+} do not behave similarly in their crystal chemistry, even though they belong to the same group in the periodic table and have almost identical ionic radii, and should show similarities analogous to Zr-Hf and Mo-W. Other differences in behaviour between technetium and rhenium have been described in the literature. Especially noteworthy is their difference in chloride formation. While rhenium is known to form only the penta and trichlorides, technetium forms only the hexa and tetrachlorides.⁽²⁴⁾

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Note added in proof: The poorly-crystallized, oxygen-rich technetium metal phases (prepared by thermal decomposition of NH_4TcO_4 in a flow of hydrogen at 230-300°C for 1 or 2 days) have in their X-ray patterns a very broad hump centred at 2.15 Å in addition to the Tc metal peaks, thus indicating the presence of an amorphous phase. Sometimes the intermediate scheelite phase can be detected in these metal phases, indicating incomplete decomposition. Although it was assumed above that the higher *d*-spacings were due to interstitial oxygen, it now appears that the possibility of interstitial nitrogen or hydrogen cannot be excluded.

Recent work by MONTMORY et al. [Bull. Soc. Franc. Miner. Crist. 86, 434 (1963)] suggests that the NaSbO₃ pyrochlore reported by SCHREWELIUS (18) actually corresponds more nearly to the composition Na₂Sb₂O₅(OH)₂. It is not impossible that our PbTcO₃ pyrochlore may likewise be off the indicated stoichiometry.

From two recent detailed studies of the decomposition of NH₄ReO₄ [P. GIBART, K. TRAORE and F. BRENET, C. R. Acad. Sci. Paris 256, 1296 (1963); P. GIBART, Bull. Soc. Chim. France 70, (1964)] it appears that thermal decomposition at low temperatures (285°) first yields an X-ray amorphous phase but which on subsequent heat treatment at 300°C yields a scheelite type phase. Unlike its technetium analogue this rhenium scheelite phase does not persist at temperatures above 400°C.

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