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Abstract

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ON SCANDIUM CHALCOGENIDES

Scandium chalcogenides, with the exception of the oxide, have been completely unstudied. The literature contains only data on the preparation of scandium sesquisulfide Sc_2S_3 (^{1}) and scandium selenide Sc_2Se_3 (^{2}). We have previously described methods of preparation and the crystal structures of scandium sesquiselenide (Sc_2Se_3) and scandium telluride (Sc_2Te_3) (^{3}). In the Sc–Te system, in addition to Sc_2Te_3, a compound of composition ScTe was found, characterized by an individual set of interplanar spacings.

The present article gives the results of an X-ray study of Sc_2O_3, Sc_2S_3, and also scandium telluride of composition ScTe. In the Sc–S and Sc–Se systems, individual compounds of composition 1 : 1 were not found. Scandium oxide of purity $> 99.9\%$, obtained from technical oxide by methods of rhodanide extraction and precipitation of scandium oxalate (^{4}), was used for the investigation. Sc_2S_3 and ScTe were synthesized from the elements. Metallic scandium of 97–97.5% purity was obtained by reduction of anhydrous scandium chloride with metallic calcium (^{5}). Sulfur, free of selenium, was first melted and purified by vacuum sublimation (10^{-4}–10^{-5} mm Hg) at 100–110°C. The purity of the sublimed sulfur was $> 99.9\%$. Tellurium of purity $> 99.99\%$ was obtained from the technical product by double reprecipitation of tellurium dioxide (^{6}) and by sublimation of preliminarily reduced and melted elemental tellurium in vacuum (10^{-4}–10^{-5} mm Hg) at 400° (^{7}).

The synthesis of Sc_2S_3 and ScTe was carried out as follows. Metallic scandium and the corresponding chalcogen, taken in equivalent amounts, were thoroughly mixed and placed in quartz ampoules of about 10 ml volume, which were then evacuated to 10^{-4} mm Hg and sealed. The weight of the mixtures was 3–5 g. The time of synthesis and annealing of the compounds was:

Sc_2S_3 temp., °C	Sc_2S_3 heating duration, h	ScTe temp., °C	ScTe heating duration, h
20–120	4	20–400	1
120–150	6	400	4
150–450	6	400–500	6
450	2	500–1000	1
450–1000	1	1000	6

Sc_2S_3 temp., °C	Sc_2S_3 heating duration, h	ScTe temp., °C	ScTe heating duration, h
1000	6		

Sc_2S_3 and ScTe are unmelted crystalline powders, yellow and black in color, respectively.

X-ray photographs of samples of Sc_2O_3, Sc_2S_3, and ScTe were taken by the powder method with filtered CuK_α radiation in RKD-57 and RKU-86 cameras. The line intensities were estimated visually on a five-point scale. The results of the X-ray analysis are presented in Tables 1, 2, and 3.

Table 1

Results of X-ray analysis of scandium oxide

Line No.	Intensity	hkl	Interplanar spacings d, kX: found	Interplanar spacings d, kX: calculated at $a = 9.835$ kX	a, kX found
1	3	211	4,014	4,015	9,833
2	5	222	2,835	2,839	9,822
3	2	400	2,456	2,459	9,827
4	2	332	2,094	2,097	9,822
5	1	521	1,793	1,795	9,822
6	5	440	1,736	1,739	9,822
7	1	530; 433	1,687	1,687	9,835
8	2	532; 611	1,595	1,596	9,834
9	1	620	1,554	1,555	9,829
10	3	541	1,516	1,518	9,824
11	3	622	1,481	1,483	9,822
12	2	631	1,451	1,450	9,840
13	1	444	1,418	1,420	9,825
14	1	710; 550; 543	1,389	1,391	9,825
15	1	640	1,362	1,364	9,822
16	1	721; 633; 552	1,338	1,338	9,835
17	1	642	1,315	1,314	9,840
18	1	732; 651	1,250	1,249	9,840
19	1	800	1,228	1,229	9,822

Line No.	Intensity	hkl	Interplanar spacings d, kX: found	Interplanar spacings d, kX: calculated at $a = 9.835$ kX	a, kX found
20	1	741; 811; 554	1,211	1,211	9,835
21	1	820; 644	1,192	1,193	9,831
22	1	653	1,175	1,176	9,831
23	1	660; 822	1,158	1,159	9,829
24	1	831; 750; 743	1,143	1,143	9,835
25	2	662	1,128	1,128	9,835
26	1	840	1,100	1,100	9,835
27	1	921; 761; 655	1,061	1,061	9,835
28	1	930; 851; 754	1,027	1,027	9,835
29	1	763; 932	1,013	1,014	9,827
30	2	844	1,004	1,004	9,835
31	1	941; 853; 770	0,9934	0,9936	9,833
32	1	860; 10, 0,0	0,9831	0,9836	9,831
33	2	862; 10, 2,0	0,9641	0,9645	9,831
34	1	666; 10, 2,2	0,9465	0,9465	9,835
35	1	952; 10, 3,1; 765	0,9376	0,9378	9,833
36	1	871; 855; 774	0,9209	0,9213	9,831
37	1	864; 10, 4,0	0,9135	0,9133	9,838
38	1	961; 10, 3,3	0,9053	0,9055	9,833
39	1	10, 4,2	0,8976	0,8978	9,833
40	1	11, 1,0; 954; 873	0,8902	0,8904	9,833
41	2	10, 5,1; 11, 2,1; 963	0,8766	0,8762	9,840

Line No.	Intensity	hkl	Interplanar spacings d, kX: found	Interplanar spacings d, kX: calculated at $a = 9.835$ kX	a, kX found
42	1	882; 10, 4,4	0,8559	0,8561	9,833
43	1	10, 5,3; 11, 3,2; 972; 776	0,8502	0,8498	9,840
44	1	866; 10, 6,0	0,8437	0,8433	9,840
45	1	875; 11, 4,1	0,8377	0,8373	9,840
46	1	10, 6,2	0,8310	0,8312	9,833
47	1	884; 12, 0,0	0,8198	0,8196	9,838
48	1	981; 12, 1,1; 11, 5,0; 11, 4,3; 974	0,8138	0,8140	9,833
49	1	12, 2,0	0,8085	0,8085	9,835
50	1	10, 7,1; 11, 5,2; 10, 5,5	0,8030	0,8032	9,833
51	2	10, 6,4; 12, 2,2	0,7978	0,7978	9,835
52	2	10, 7,3; 11, 6,1	0,7824	0,7825	9,933
53	2	12, 4,0	0,7775	0,7775	9,835

$a_{\text{av}} = 9.835 \pm 0.005$ kX

Table 2

Results of X-ray analysis of scandium sulfide

Line No.	Intensity	hkl	Interplanar spacings d, kX: found	Interplanar spacings d, kX: calculated at $a = 10.37$, $c = 31.11$ kX
1	2	113?	5,83	5,99
2	1	115	4,78	4,75
3	2	222	3,57	3,57
4	1	208	3,11	3,11
5	1/2	226	3,00	2,99
6	5	400	2,60	2,59
7	1/2	402	2,555	2,557
8	1/2	2,2,10	2,370	2,372
9	1/2	424	2,217	2,222
10	1/2	*	2,182	–
11	1	2,2,12?	2,099	2,116
12	1	511	2,031	2,030
13	1	428	1,990	1,992
14	1	2,2,14	1,896	1,900
15	5	440	1,833	1,833
16	1	519	1,761	1,753
17	1	3,3,13	1,711	1,710
18	2	4,0,14	1,686	1,687
19	1/2	622	1,629	1,630
20	1/2	3,3,15	1,581	1,581
21	1/2	*	1,528	–
22	5	4,4,12	1,497	1,497
23	1	1,1,21	1,451	1,452
24	1	644	1,413	1,414
25	1/2	*	1,374	–
26	5	800	1,296	1,296
27	1/2	739	1,262	1,267
28	1/2	4,0,22	1,241	1,241

* The origin of the line has not been established.

All lines of the scandium oxide photograph are satisfactorily indexed in a cubic body-centered lattice of the Mn_2O_3 type (8) with $a = 9.835 \pm 0.005$ kX, $Z = 16$. According to literature data (9–11), the lattice parameter of Sc_2O_3 is somewhat smaller: from 9.76 to 9.828 kX (see Table 4). The X-ray density of scandium oxide is 3.84 g/cm^3; the pycnometric density is 3.75 g/cm^3.

The lines of the scandium sulfide photograph, in intensity, are sharply divided into two categories: very strong and weak. The strong lines are indexed in a primitive cubic lattice with $a_0 = 2.591$ kX, which is a subcell. The weak lines, however, are due to a superstructure. By analogy with the recently

Table 3

Results of X-ray analysis of scandium telluride of composition ScTe

Line No.	Intensity	*hkl*	Interplanar spacings *d*, kX: found	Interplanar spacings *d*, kX: calculated for $a = 4.122$, $c = 6.735$ kX	Line No.	Intensity	*hkl*	Interplanar spacings *d*, kX: found	Interplanar spacings *d*, kX: calculated for $a = 4.122$, $c = 6.735$ kX
1	1	002	3.38	3.37	14	1	212	1.253	1.253
2	5	101	3.167	3.155	15	1	204	1.226	1.225
3	4	102	2.458	2.450	16	2	300	1.189	1.190
4	4	110	2.060	2.061	17	2	213	1.156	1.156
5	3	103	1.903	1.900	18	1	302	1.121	1.122
6	2	112	1.757	1.758	19	2	205	1.075	1.075
7	2	201	1.728	1.726	20	1	220	1.031	1.031
8	1	004	1.683	1.683	21	1	222	0.9834	0.9854
9	2	202	1.580	1.577	22	1	311	0.9777	0.9796
10	2	203	1.399	1.397	23	1	304	0.9708	0.9717
11	2	211	1.323	1.323	24	2	206	0.9500	0.9502
12	2	144	1.303	1.304	25	1	313	0.9050	0.9059
13	2	105	1.261	1.260					

Table 4

Some properties of scandium chalcogenides

Compound	Color	Density, g/cm^3: pycnometric	Density, g/cm^3: X-ray	Crystal lattice	Lattice type	Z	Lattice parameters, kX
Sc_2O_3	White	3.70	3.84	Cubic body-centered	Mn_2O_3	16	$a = 9.76$ (9) $a = 9.79$ (10) $a = 9.825$ (11) $a = 9.835 \pm 0.005$
Sc_2S_3	Yellow	2.80	2.96	Tetragonal face-centered	β-In_2S_3	32	$a = 10.37 \pm 0.01$ $c = 31.11 \pm 0.03$ $c/a = 3$
Sc_2Se_3	Brown-violet	4.51	4.55	Cubic face-centered	γ'-Al_2O_3	1 1/3	$a = 5.405 \pm 0.005$
Sc_2Te_3	Black	5.26	5.32	Cubic face-centered	γ'-Al_2O_3	1 1/3	$a = 5.805 \pm 0.005$
ScTe	Black	5.65	5.75	Hexagonal	NiAs	2	$a = 4.122 \pm 0.005$ $c = 6.735 \pm 0.005$ $c/a = 1.634$

With the established structure β-In_2S_3 (^{12}), for Sc_2S_3 we adopted a tetragonal face-centered lattice with $a = 10.37 \pm 0.01$ kX ($a = a_0 \times 4$) and $c = 31.11 \pm 0.03$ kX; $c/a = 3$, $Z = 32$. Indeed, of 24 weak lines up to angles $\theta \approx 40°$, 21 lines are satisfactorily indexed in such a tetragonal lattice. The presence of unindexed lines can be explained by the existence of another superstructure in scandium sulfide or by the presence of small amounts of foreign impurities. The X-ray density calculated for such a tetragonal lattice proved to be 2.96 g/cm^3; the density of Sc_2S_3, determined pycnometrically with chloroform, is 2.80 g/cm^3; according to the literature it is 2.85 g/cm^3 (^{1}).

All 25 lines of the ScTe pattern are well indexed in a hexagonal lattice of the NiAs type with $a = 4.112 \pm 0.005$ kX and $c = 6.735 \pm 0.005$ kX, $c/a = 1.634$, $Z = 2$.

The X-ray density of ScTe is 5.75 g/cm^3; the pycnometric density, found using bromoform, is 5.65 g/cm^3.

The results obtained by us do not agree with the data of a recently published work (^{13}), in which it is indicated that ScTe crystallizes in a hexagonal lattice with $a = 6.728$ Å and $c = 8.360$ Å. The type of crys-

of the gallic lattice Z, and the density of ScTe is also not reported in this work.

The properties of the scandium chalcogenides currently known are presented in Table 4. It should be noted that the color of the compounds changes regularly from white to black in accordance with the increase in the polarizability of the chalcogen, and the crystal lattices of all scandium chalcogenides are characterized by high symmetry.

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Note: Figure translations are in progress. See original paper for figures.

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