TABLE I

X-RAY DIFFRACTION PATTERN OF TETRAGONAL Al_2S_3

	$a = 7.028 \pm 0.001$ Å					$c = 29.811 \pm 0.006$ Å			
$h\ k\ l$	d_{calc}	d_{obsd}	I_{calc}	I_{obsd}	$h\ k\ l$	d_{calc}	d_{obsd}	I_{calc}	I_{obsd}
0 0 4	7.4528	7.4378	27	46	3 1 2	2.1983		9	
1 0 1	6.8408	6.8530	31	36	3 0 5	2.1805	2.1802	19	32
1 0 3	5.7382	5.7325	394	425	1 0 13	2.1801		4	
1 1 2	4.7147	4.7060	24	83	3 1 4	2.1299	2.1292	17	13
1 0 5	4.5467	4.5576	16	21	2 2 8	2.0674		5	
0 0 8	3.7264	3.7330	12	30	3 0 7	2.0527	2.0537	1	30
1 0 7	3.6423	3.6223	28	20	2 1 11	2.0525		20	
1 1 6	3.5137	3.4991	73	77	3 1 6	2.0288	2.0310	23	38
2 0 2	3.4204	—	< 1	–	2 0 12	2.0286		11	
2 0 4	3.1786	—	6	–	1 1 14	1.9573	1.9445	8	17
2 1 1	3.1259	—	16	–	3 2 1	1.9452		5	
2 1 3	2.9968	3.0005	390	587	3 2 3	1.9129		207	
1 0 9	2.9963		141		3 0 9	1.9127	1.9128	11	588
2 0 6	2.8691	2.8707	730	757	1 0 15	1.9124		122	
2 1 5	2.7805	—	2	–	3 1 8	1.9088		15	
2 0 8	2.5566	2.5556	13	24	0 0 16	1.8632		1	
1 1 10	2.5565		2		3 2 5	1.8528	1.8527	16	12
2 1 7	2.5290	2.5318	4	37	2 1 13	1.8525		1	
1 0 11	2.5286				2 0 14	1.8211	—	< 1	
2 2 0	2.4849	2.4844	1000	1286	3 1 10	1.7819		3	
0 0 12	2.4843		495		3 2 7	1.7725	1.7783	3	29
2 2 4	2.3573	—	1	–	3 0 11	1.7724		< 1	
3 0 1	2.3356	—	2	–	4 0 0	1.7571	1.7555	424	1284
3 0 3	2.2803	—	1	–	2 2 12	1.7569		835	
2 1 9	2.2800	—	< 1	–	4 0 2	1.7450	—	< 1	–
2 0 10	2.2733	—	< 1	–	4 0 4	1.7102	—	3	–
3 1 0	2.2226	—	< 1	–	4 1 1	1.7109	—	< 1	–
1 0 17	1.7014	—	< 1	–	4 2 8	1.4481		3	
4 1 3	1.6801		17		3 3 10	1.4480	1.4476	1	18
3 2 9	1.6800	1.6796	14	57	4 1 11	1.4429		2	
2 1 15	1.6798		30		4 0 12	1.4345	1.4349	240	322
4 0 6	1.6566	—	< 1	–	3 1 16	1.4278		3	
3 1 12	1.6564	—	< 1	–	4 3 1	1.4041	—	< 1	–
3 3 2	1.6465	—	2	–	5 0 1	1.4041	—	< 1	–
2 0 16	1.6461	—	< 1	–	3 0 17	1.4039	—	< 1	–
4 1 5	1.6390	—	1	–	2 1 19	1.4038	—	< 1	–
3 0 13	1.6388	—	1	–	5 0 3	1.3918		15	
4 0 8	1.5893	—	2	–	4 3 3	1.3918		< 1	
4 1 7	1.5826	—	4	–	3 2 15	1.3917	1.3917	37	79
3 2 11	1.5825	—	4	–	3 0 21	1.3915		< 1	
3 3 6	1.5716	—	3	–	4 2 10	1.3902		< 1	
1 1 18	1.5712	—	3	–	5 1 2	1.3725	—	2	–
4 2 2	1.5629	—	< 1	–	2 0 20	1.3722	—	2	–
4 2 4	1.5378	1.5323	4	25	4 3 5	1.3682	—	5	–
3 1 14	1.5376		6		5 0 5	1.3682	—	< 1	–
2 1 17	1.5314		10		4 1 13	1.3681	—	2	–
1 0 19	1.5313		1		5 1 4	1.3554	—	2	–
4 1 9	1.5157	1.5156	32	74	4 0 14	1.3553		< 1	
3 0 15	1.5156		27		5 0 7	1.3348		5	
4 0 10	1.5137		< 1		4 3 7	1.3348		< 1	
4 2 6	1.4984	1.4988	81	291	5 1 6	1.3282	1.3285	8	28
2 0 18	1.4981		35		4 2 12	1.3281		9	
2 2 16	1.4907		3		3 1 18	1.3280		8	
0 0 20	1.4906		1						
3 2 13	1.4852		1						

Reactions were run at pressures of 1, 2, and 3 kb at 1000°C, hold 3 hr, cool 3 hr to 700°C, and quenched. The products were washed with CS_2 to remove excess S, leaving yellow-orange crystalline material. The Guinier x-ray diffraction patterns of the products of reactions run at 2 kb and 3 kb were similar and could be indexed on the basis of cubic unit cells $a = 9.938 \pm 0.001$ Å in which only 16 of 24 reflections were used. The pattern was completely indexed when a tetragonal cell was used similar to that of β-In_2S_3 in which a tetragonal = a cubic/$\sqrt{2}$ and c tetragonal = $3a$ cubic. The refined parameters are $a = 7.026 \pm 0.001$, $c = 29.819 \pm 0.001$ Å. In order to prove that the structure is similar to that of βIn_2S_3, intensities of the powder diffraction pattern were calculated (*9*) and compared to observed intensities. Intensities were gathered by tracing the peaks of a diffractometer pattern on to Cronaflex® drafting film No. IDF4, cutting out the peaks and weighing them. The diffractometer chart was obtained using a Norelco diffractometer with a bent crystal monochromator and CuKα radiaton. Background was estimated by drawing a smooth curve. For the calculated intensities, position parameters reported for β-In_2S_3 were used (*4*). No attempt was made to refine the parameters. The R factor defined as $R = |I_{obsd} - I_{calc}|/I_{obsd}$ is 17% which is sufficient to establish the similarity of the structure. The data are shown in Table I.

The product of the reaction run at 1 kb did not show the spinel type phase; thus, the pressure necessary for formation at 1000°C. is somewhere between 1 and 2 kb. A reaction run at 1200°C, 65 kb, 10 min, cool to 1000°C., slow cool 3 hr to 700°C yielded a spinel type phase similar to that prepared at 2 kb. Good crystal growth occurred, and electrical resistivity measurements were made on a crystal. The resistivity showed semiconducting behavior $\rho_{0.298°K} = 1 \times 10^9$ Ωcm with an activation energy $E_a = 0.3$ eV.

B. $MnAl_2S_4$

A reaction starting with the elements in the ratio 2Al/Mn/5S at 1000°C, 3 kb held for 5 hr, cool 3 hr to 700°C, and quench yielded a mixture of phases. After washing with CS_2 and 1:1 HCl, orange crystals remained which gave a spinel type powder diffraction pattern $a = 10.052 \pm 0.001$ Å. The best samples of the compound were formed at higher pressure. The reaction of 2Al/Mn/4S at 1200°C, 65 kb, held 1 hr, cool 3 hr to 1000°C, and quench yielded orange and green material. The orange material showed a spinel type diffraction pattern, $a = 10.092$ Å, while the green material showed the cubic α-MnS pattern. The density of the crystals was measured by a displacement technique in bromoform. Found 2.95 g/cm^3; calculated for $MnAl_2S_4$: 3.06 g/cm^3. It is apparent that the compound tolerates a large degree of nonstoichiometry.

Two reactions run at 30 kb, 1000°C hold 2 hr, quench, and starting with the reagents 0.5 MnS/-2Al/3S and 0.25 MnS/2Al/3S yielded nearly homogeneous products. The spinel type unit cell dimensions are $a = 10.050 \pm 0.001$ Å and $a = 10.010$ Å respectively, again illustrating nonstoichiometry.

Magnetic and electrical measurements were made on a sample prepared at 1000°C and 45 kb, held 2 hr/Q. The unit cell was refined to $a = 10.052$ Å, and a trace of α-MnS was seen in the powder pattern. Resistivity measurements were made on a polycrystalline piece and showed semiconducting behavior $\rho_{298°K} = 1.2 \times 10^{10}$ Ωcm, $E_a = 0.7$ eV. The magnetic measurements showed paramagnetic behavior from 77–300°K, with $C = 16.5 \times 10^{-3}$ emu °K/gOe and $\theta = -116$°K. Assuming the formula $MnAl_2S_4$, $\mu^2_{eff} = 31.4$ μB^2/f wt. $\pm 2\mu B^2$/f wt. When μ^2_{eff} is calculated for $MnAl_2S_4$ using the formula for electron spin only and assuming high spin Mn^{2+}, then it is 35 μB^2/f wt. The difference is consistent with the observed nonstoichiometry.

Acknowledgments

Dr. T. A. Bither and Dr. A. W. Sleight are thanked for helpful discussions. Magnetic measurements were made by Mrs. C. G. Frederick. Resistivity measurements were made by Mr. J. L. Gillson. Guinier camera patterns were taken by Miss M. S. Licis. Mr. C. L. Hoover is thanked for supervision of high pressure experiments.

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