

High-Pressure Spinel Type Al_2S_3 and MnAl_2S_4

P. C. DONOHUE

Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Received September 20, 1969

New spinel type forms of Al_2S_3 and MnAl_2S_4 were prepared at pressures from 2 to 65 kb. The Al_2S_3 was shown to exhibit a structure similar to $\beta\text{-In}_2\text{S}_3$ in which ordered vacancies result in a super lattice with a tetragonal cell. The cell dimensions are $a = 7.026 \pm 0.001 \text{ \AA}$, $c = 29.819 \pm 0.001 \text{ \AA}$. Electrical measurements show semi-conducting behavior with $\rho_{298^\circ\text{K}} = 10^9 \ \Omega \text{ cm}$, $Ea = 0.3 \text{ eV}$. The spinel form of MnAl_2S_4 exhibits a range of stoichiometry as indicated by a range of cell dimension from $a = 10.092 \pm 0.001 \text{ \AA}$ to $a = 10.010 \pm 0.001 \text{ \AA}$. Resistivity and magnetic measurements indicate semiconducting and paramagnetic behavior.

Introduction

The compound Al_2S_3 is known to form three polymorphs (1): a hexagonal α form, a related hexagonal β form that has a defect wurtzite-type structure, and a γ form having the corundum type structure. The coordination of Al in the α and β forms is tetrahedral, while it is octahedral in the corundum type. These are prepared at ambient pressure. A cubic spinel-type ($a = 9.93 \pm 0.1 \text{ \AA}$) Al_2S_3 is reported (2) to form when 2 at. % As is substituted for Al. The β form of indium sesquisulfide is known as a defect spinel-type structure (3, 4). It contains ordered vacancies that result in a superlattice; consequently, the unit cell dimensions are $a = 7.61$, $c = 32.24 \text{ \AA}$.

A large series of thiospinel compounds is known; however, the compound MnAl_2S_4 is reported to form a rhombohedral structure when prepared at ambient pressure (5). In this study the systems Al_2S_3 and MnAl_2S_4 were studied at high pressure.

Experimental

Reactions to prepare Al_2S_3 were carried out, starting with 4N purity Al powder, 50/200 mesh, and sulfur of 6N purity. To prepare MnAl_2S_4 , the same reagents and either MnS or Mn and S were used.

Experiments run at 3000 atm or less were done in a vessel pressurized with compressed argon and internally heated by a platinum resistance furnace. The reactants were sealed *in vacuo* in heavy walled

Pyrex[®] tubing (9-mm o.d., 6-mm i.d.) that was contained in a platinum jacket. The Pyrex is soft at 700°C and translates the pressure while acting as an inert container. Reaction cycles were typically as follows: 200 atm, heat to 700°C, increase pressure to 3000 atm or less, increase temperature to 1000°C, hold for the desired length of time, program cool, and quench. Quenching is cooling from operating temperature to room temperature in about five minutes. Reactions done at pressures higher than 3000 atm were performed in a tetrahedral anvil press of National Bureau of Standards design (6). The operating procedure has been described elsewhere (7).

The products of all reactions were studied by x-ray powder diffractometry using Debye-Scherrer and Guinier techniques. Unit cell dimensions were refined using a computerized least-squares technique.

Resistivity measurements were done by a four probe technique described elsewhere (8). Magnetic susceptibility measurements were made using a vibrating sample magnetometer in fields of 16 kOe at temperatures from 77-298°K.

Results and Discussion

A. Al_2S_3

The elements were mixed in the ratio of 1Al:2S since excess S was found to enhance crystal growth and impede reaction of Al with the Pyrex tube.

TABLE I
X-RAY DIFFRACTION PATTERN OF TETRAGONAL Al_2S_3

| $a = 7.028 \pm 0.001 \text{ \AA}$ | | | | | $c = 29.811 \pm 0.006 \text{ \AA}$ | | | | |
|-----------------------------------|-------------------|-------------------|-------------------|-------------------|------------------------------------|-------------------|-------------------|-------------------|-------------------|
| $h k l$ | 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 | | 390 | | 3 2 3 | 1.9129 | | 207 | |
| 1 0 9 | 2.9963 | 3.0005 | 141 | 587 | 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 | | 13 | | 0 0 16 | 1.8632 | | 1 | |
| 1 1 10 | 2.5565 | 2.5556 | 2 | 24 | 3 2 5 | 1.8528 | 1.8527 | 16 | 12 |
| 2 1 7 | 2.5290 | | 4 | | 2 1 13 | 1.8525 | | 1 | |
| 1 0 11 | 2.5286 | 2.5318 | 4 | 37 | 2 0 14 | 1.8211 | — | < 1 | |
| 2 2 0 | 2.4849 | | 1000 | | 3 1 10 | 1.7819 | | 3 | |
| 0 0 12 | 2.4843 | 2.4844 | 495 | 1286 | 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 | | 4 | | 4 3 5 | 1.3682 | — | 5 | — |
| 3 1 14 | 1.5376 | | 6 | | 5 0 5 | 1.3682 | — | < 1 | — |
| 2 1 17 | 1.5314 | 1.5323 | 10 | 25 | 4 1 13 | 1.3681 | — | 2 | — |
| 1 0 19 | 1.5313 | | 1 | | 5 1 4 | 1.3554 | — | 2 | — |
| 4 1 9 | 1.5157 | | 32 | | 4 0 14 | 1.3553 | | < 1 | |
| 3 0 15 | 1.5156 | 1.5156 | 27 | 74 | 5 0 7 | 1.3348 | | 5 | |
| 4 0 10 | 1.5137 | | < 1 | | 4 3 7 | 1.3348 | | < 1 | |
| 4 2 6 | 1.4984 | | 81 | | 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 | 1.4988 | 3 | 291 | 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 CS₂ 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 -In₂S₃ 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 β In₂S₃, 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 CuK α radiation. Background was estimated by drawing a smooth curve. For the calculated intensities, position parameters reported for β -In₂S₃ were used (4). No attempt was made to refine the parameters. The R factor defined as $R = |I_{\text{obsd}} - I_{\text{calc}}|/I_{\text{obsd}}$ 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 $\rho_{0.298^\circ\text{K}} = 1 \times 10^9$ Ωcm with an activation energy $E_a = 0.3$ eV.

B. MnAl₂S₄

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 CS₂ 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/cm³; calculated for MnAl₂S₄: 3.06 g/cm³. 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 $\rho_{298^\circ\text{K}} = 1.2 \times 10^{10}$ 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 $\theta = -116^\circ\text{K}$. Assuming the formula MnAl₂S₄, $\mu_{\text{eff}}^2 = 31.4$ $\mu\text{B}^2/\text{f wt.}$ $\pm 2\mu\text{B}^2/\text{f wt.}$ When μ_{eff}^2 is calculated for MnAl₂S₄ using the formula for electron spin only and assuming high spin Mn²⁺, then it is 35 $\mu\text{B}^2/\text{f wt.}$ 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.

References

1. J. FLAHAUT, *Ann. Chim. Paris* **7**, 632 (1952).
2. H. SCHÄFER, G. SCHÄFER, AND A. WEISS, *Z. Anorg. Chem.* **325**, 77 (1963).
3. C. J. M. ROOYMANS, *J. Inorg. Nucl. Chem.* **11**, 78 (1959).
4. G. A. STEIGMANN, H. H. SUTHERLAND, AND J. GOODYEAR, *Acta Cryst.* **19**, 967 (1965).
5. J. FLAHAUT, *C. R. Acad. Sci. Paris* **233**, 1279 (1951).
6. E. C. LLOYD, U. O. HUTTON, AND D. P. JOHNSON, *J. Res. Natl. Bur. Std.* **C63**, 59 (1959).
7. T. A. BITHER, C. T. PREWITT, J. L. GILLSON, P. E. BIERSTEDT, R. B. FLIPPEN, AND H. S. YOUNG, *Solid State Commun.* **4**, 533 (1966).
8. T. A. BITHER, J. L. GILLSON, AND H. S. YOUNG, *Inorg. Chem.* **5**, 1559 (1966).
9. W. K. JEITSCHKO AND E. PARTHÉ, Unpublished computer program for calculation of x-ray powder diffraction patterns.