

High-Pressure Phase Transformations in MnAl_2S_4 and MnGa_2S_4

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Phase transformations in MnAl_2S_4 and MnGa_2S_4 have been investigated at high pressure up to 95 kb and temperature up to 1000°C. The decomposition of MnAl_2S_4 to MnS with rock salt structure and the spinel phase at moderately high pressure has been observed. The lattice parameter for the spinel phase is shown to decrease with increasing pressure. It is interpreted due to the formation of nonstoichiometric spinel expressed by $\text{Mn}_{1-x}\text{Al}_2\text{S}_{4-x}$. Above about 90 kb, an Al-rich unknown phase appears instead of spinel, which can not be identified on account of its extreme unstableness in air.

Six polymorphs have been observed for MnGa_2S_4 , designated as I ~ VI in the order of increasing pressure. MnGa_2S_4 IV is identified to be identical with an atmospheric pressure phase of MnAl_2S_4 with the ZnIn_2S_4 structure. The crystal structures of MnGa_2S_4 I, II and III are thought to be due to the polytypism in the ZnIn_2S_4 structure. The identification of the other two polymorphs can not be made.

Introduction

Sulfides frequently crystallize in quite different crystal structures from those of corresponding oxides because of the smaller electronegativity and the larger ionic radius of sulfur ions. For example, NiAs type, Th_3P_4 type, and CaY_2S_4 type are not known in oxides. It was shown that the structure types in sulfides can not be understood only by the ionic radius ratio (I), which is found to be a very useful measure for the crystal chemistry of oxides. It may be expected, therefore, that the high pressure phase transformations of sulfides occur in a somewhat different way from the case of oxides.

In the present study, the high-pressure transformation in MnAl_2S_4 and MnGa_2S_4 has been studied. MnAl_2S_4 has the layer structure typified by ZnIn_2S_4 (2, 3) which do not appear in the case of oxides. The lattice is constituted with the layers of sulfur atoms in a mixed close-packed arrangement with the packing sequence of (ABCACABCBCAB) along the c axis. Metallic atoms are in the holes of this packing. Each zinc atom is tetrahedrally surrounded by sulfur atoms. The In (2) atoms also are tetrahedrally coordinated and the In (I) atoms

are octahedrally coordinated. No cation exists in holes at every fourth layer along the c axis. As for MnGa_2S_4 , which is gallium substitute of MnAl_2S_4 , the crystal structure of an atmospheric pressure phase is not known. It is very interesting to know the difference between the crystal structure for high-pressure phases of MnGa_2S_4 and MnAl_2S_4 , since both gallium and aluminium belong to the third group of the Periodic System.

Experimental

High-pressure and high-temperature experiments were carried out with a tetrahedral anvil-type high pressure apparatus, using the pyrophyllite tetrahedron as pressure-transmitting material. The tungsten carbide anvils with the edge length of 9, 15, and 30 mm were used, covering the pressure range from 10 to 95 kb in the present study. Pressures were determined at room temperature by measuring electrical resistance for phase transformations of Bi (I-II) at 26 kb, Ba (I-II) at 55 kb, Bi (III-V) at 77 kb and Sn (I-II) at 100 kb. A graphite tube was used as a sample container and a heating element. A special sample container made of thin gold foil with 30μ thickness was also used in certain runs for MnAl_2S_4 for keeping off the contamination. Temperature was measured with Pt/Pt-13%Rh thermocouple without

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TABLE I
POWDER DIFFRACTION DATA FOR ZnIn_2S_4 -TYPE STRUCTURE

MnAl_2S_4 I ^a				MnGa_2S_4 IV ^b			
<i>hkl</i>	<i>d</i> _{obsd}	<i>d</i> _{calcd}	<i>I</i>	<i>hkl</i>	<i>d</i> _{obsd}	<i>d</i> _{calcd}	<i>I</i>
00 9	4.039	4.032	6	00 6	6.124	6.058	1
10 1	3.178	3.188	5	00 9	4.053	4.039	5
10 2	3.153	3.152	6	10 2	3.164	3.152	5
00 12	3.017	3.024	3	00 12	3.019	3.029	2
10 7	2.719	2.724	4	10 7	2.725	2.724	2
10 8	2.613	2.615	4	10 8	2.625	2.616	2
10 11	2.297	2.297	1	00 18	2.020	2.019	1
10 13	2.104	2.104	2	11 0	1.848	1.848	10
11 0	1.848	1.848	10	11 9	1.678	1.680	2
10 17	1.777	1.776	8				
11 9	1.681	1.680	3				
$a = 3.696 \pm 0.002 \text{ \AA}$				$a = 3.695 \pm 0.003 \text{ \AA}$			
$c = 36.29 \pm 0.02 \text{ \AA}$				$c = 36.35 \pm 0.05 \text{ \AA}$			
$V = 429.3 \pm 0.7 \text{ \AA}^3$				$V = 429.8 \pm 1.3 \text{ \AA}^3$			

^a Atmospheric pressure phase.

^b Prepared at 70 kb and 600°C.

any correction for the pressure effect on the thermal emf.

Pressure was applied to the sample first, then temperature was brought to the desired value, and held for a sufficient time duration for an equilibrium (e.g., 15 min at 1000°C, 30 min at 800°C, and 40–60 min at 600°C). The furnace power was then turned off quickly and the assembly allowed to cool to ambient temperature before pressure was released. The quenched specimen was examined by the powder X-ray diffraction technique and microscopic observation.

The starting materials for high-pressure experiments were provided by Dr. Teruo Teranishi. These materials were prepared from the powder of the elements by the chemical transport reaction with the temperature gradient from 950 to 800°C in a crucible, using a carrier of iodine.

Results

(a) MnAl_2S_4

The crystal structure of an atmospheric pressure phase of MnAl_2S_4 is of the ZnIn_2S_4 type with the space group C_{3v}^2-R3m (2, 3). Its trimolecular unit cell was determined to have the hexagonal lattice parameters $a = 3.696 \pm 0.002 \text{ \AA}$, $c = 36.29 \pm 0.02 \text{ \AA}$, and $V = 429.3 \pm 0.7 \text{ \AA}^3$ (Table I).

Experimental results on the pressure–temperature phase diagram for MnAl_2S_4 up to 90 kb are summarized in Fig. 1. The atmospheric pressure phase, MnAl_2S_4 I, was found to decompose to two phases beyond about 15 kb. One of the two phases was found to be α -MnS with the rock salt structure, and the other to have the spinel structure. The lattice parameters were determined by using the two lines for α -MnS and five lines for spinel. The runs with the special sample container made of thin gold foil gave the same results as those with the graphite container. The lattice parameter of the spinel was found to decrease with increasing pressure, while the lattice parameter of the rock salt phase was found constant with the value of $5.223 \pm 0.005 \text{ \AA}$. Simultaneously, the relative intensity of the X-ray diffraction lines for spinel was found to decrease with pressure, while those for α -MnS increase. The variation of the lattice parameters of spinel with pressure is illustrated up to 70 kb in Fig. 2. It is to be noted that the lattice parameter of spinel varies with pressure, but it is almost independent of temperature

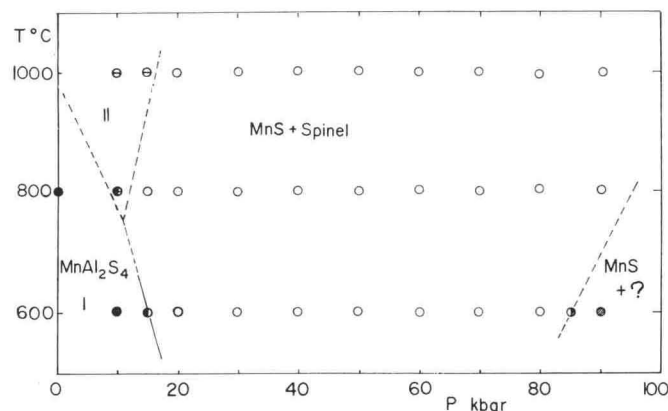


FIG. 1. Phase diagram for MnAl_2S_4 .

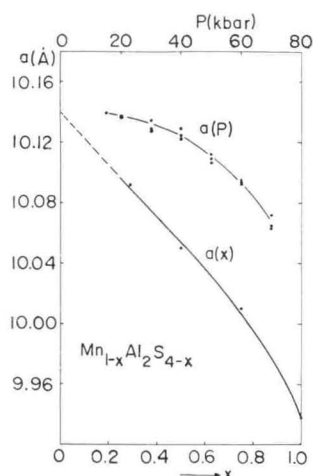


FIG. 2. The unit cell parameters of manganese aluminum sulfospinel $\text{Mn}_{1-x}\text{Al}_2\text{S}_{4-x}$ versus synthesized pressure, $a(P)$ (upper curve), in which the data for various temperatures are plotted indifferently. The lower curve $a(x)$ indicates the composition dependence of the unit cell parameter which was obtained by using the data of Donohue (5).

in this pressure region. Above 80 kb, the accurate determination of the lattice parameter became difficult, owing to the weakness of the intensity of the powder X-ray diffraction lines of the spinel. However, the estimated lattice parameter of spinel phases prepared at different temperatures did not agree with each other in this pressure region; the higher the temperature was, the larger the lattice parameter was. This fact may be related to the positive slope of the equilibrium phase boundary.

Above about 90 kb at 600°C, a new phase appeared instead of spinel. The powder X-ray diffraction

TABLE II

POWDER DIFFRACTION DATA FOR MnAl_2S_4 II^a

d_{obsd}	I/I_0
1.674	2
1.824	6
2.085	3
2.160	8
2.355	2
2.787	10
3.101	4
4.322	3

^a Prepared at 10 kb and 1000°C.

analysis revealed that the run products consist of α -MnS and the new phase. The new phase was so unstable in air, that the effort to examine the structure was unsuccessful. However, the phase was presumably taken for an Al-rich phase. In addition to these, a phase MnAl_2S_4 II was observed at around 10 kb and 1000°C and found to be a single phase by microscopic observation. Equilibrium phase boundary was not clear and no identification of this phase could be made. The obtained powder X-ray diffraction data is shown in Table II.

(b) MnGa_2S_4

Experimental results on pressure-temperature diagram for MnGa_2S_4 up to 95 kb are summarized in Fig. 3. At least six phases of MnGa_2S_4 were found in this pressure range, designating MnGa_2S_4 I ~ VI in the order of increasing pressure. MnGa_2S_4

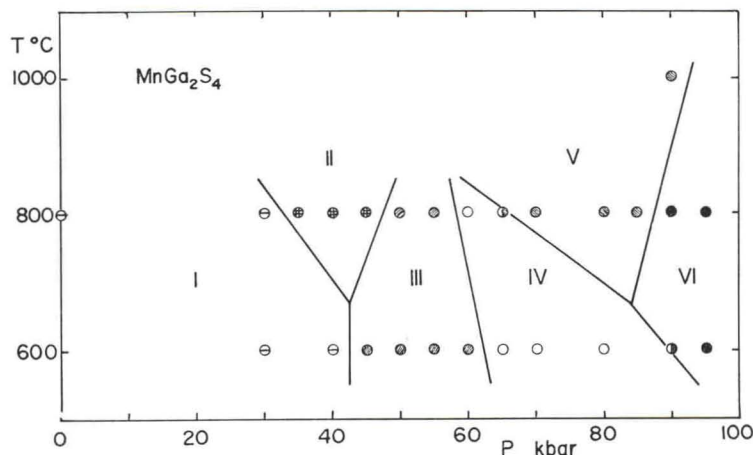


FIG. 3. Phase diagram for MnGa_2S_4 .

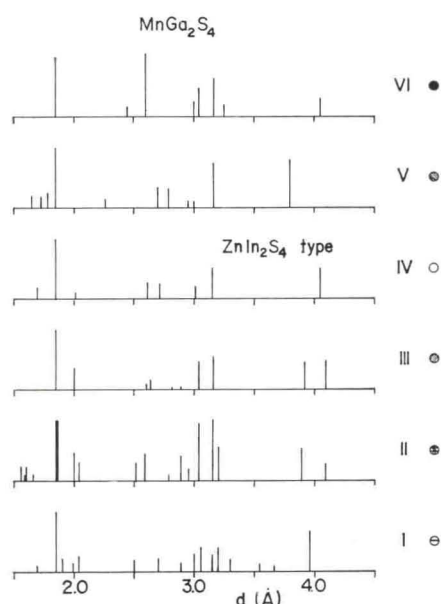


FIG. 4. Comparison of d values of six polymorphs of MnGa_2S_4 .

IV was considered to have the same crystal structure as that of MnAl_2S_4 I with the ZnIn_2S_4 structure. Its trimolecular unit cell has the hexagonal lattice parameters $a = 3.695 \pm 0.003$ Å, $c = 36.35 \pm 0.05$ Å, and $V = 429.8 \pm 1.3$ Å³. These values were slightly larger than those of MnAl_2S_4 I. The obtained crystallographic data of this phase is summarized in Table I. Three lower pressure polymorphs, MnGa_2S_4 I, II and III were found to have powder X-ray pattern similar to that of MnGa_2S_4 IV. The observed d spacings of MnGa_2S_4 I ~ VI were illustrated in Fig. 4.

In addition to these polymorphs, two other phases, MnGa_2S_4 V and MnGa_2S_4 VI, which are differing considerably in the powder X-ray pattern from those of I ~ IV phases, appeared above about 70 kb. These phases were found to be single phase by microscopic observation. The powder X-ray pattern of MnGa_2S_4 VI was not identical to that of high pressure form of In_2S_3 , as was suggested in the case of the high pressure phase of MnIn_2S_4 (I). The possibility of being α -MnS-like structure may also be excluded since the relative intensity of the reflection peak near the d value of 2.6 Å is weak. Further identification could not be made.

The runs for the reverse reaction of the high-pressure polymorphs were carried out at 30 kb and 600°C. It was observed that all polymorphs were reversibly transformed to the atmospheric pressure phase, MnGa_2S_4 I.

Discussion

It is found that MnAl_2S_4 I of the ZnIn_2S_4 type with the layer structure transforms to the spinel structure and α -MnS. This result may be explained by the increase of the coordination numbers of metal ions from (4,4,6) of the ZnIn_2S_4 type to (4,6,6) of the spinel type, being accompanied by the increase of density. The transformation in MnAl_2S_4 I at moderately high pressure is similar to the case of ZnIn_2S_4 , in which the normal spinel phase has been synthesized at 40 kb and 400°C (4). However, the systematic decrease in the lattice parameter of manganese aluminium sulfospinel with increasing pressure suggests the occurrence of dropping out of Mn ions from MnAl_2S_4 lattice and the formation of the defect spinel. Manganese aluminium sulfospinel may be expressed as $\text{Mn}_{1-x}\text{Al}_2\text{S}_{4-x}$, where x is a parameter representing an amount of exsolved MnS, which increases in proportion to the increase of pressure.

During the preparation of this manuscript, a paper of Donohue (5) which reported the synthesis of nonstoichiometric manganese aluminium sulfospinel at high pressure was brought to our attention. A mixed product of nonstoichiometric spinel and α -MnS were prepared from the powder of elements in the ratio 2Al/Mn/4S at 65 kb. Nearly homogeneous products of the nonstoichiometric spinel were observed in two reaction runs at 30 kb starting with the reagents 0.5MnS/2Al/3S and 0.25MnS/2Al/3S. This fact indicates a tolerance of a large degree of nonstoichiometry as expressed by $\text{Mn}_{1-x}\text{Al}_2\text{S}_{4-x}$. Using the data of Donohue (5), the relation between the lattice parameter of spinel and the parameter x was obtained, which is illustrated in Fig. 2. This shows that the spinel obtained at 15 kb is almost stoichiometric and the one obtained at 70 kb has x value of about 0.4. It may be considered that the spinel structure becomes unstable above about 90 kb, on account of marked dropping out of Mn ions from MnAl_2S_4 lattice.

There is no ground for the instability of aluminium sulfospinels. For example, both CdAl_2S_4 and HgAl_2S_4 were reported to transform to the cubic spinel structure from Ag_2HgI_4 -type structure of an atmospheric pressure phase (6). Relative instability in manganese aluminium sulfospinel may be related to the extra stability of α -MnS with the rock salt structure at high pressure. The fact that several manganese complex sulfides (e.g., Mn_2GeS_4 and Mn_2SiS_4 with the olivine structure) were also found to decompose at high pressure (7) supports this consideration.

In the higher-pressure region above about 90 kb, α -MnS and an Al-rich unknown phase were observed. Such decomposition scheme found in MnAl_2S_4 is similar to that found in the corresponding oxide MnAl_2O_4 , which was reported to decompose to $\text{MnO} + \text{Al}_2\text{O}_3$ at very high pressure (8).

As for MnGa_2S_4 , six polymorphs were observed in this study. Three of these polymorphs MnGa_2S_4 I, II, and III were found to have similar d spacings to those of MnGa_2S_4 IV with the ZnIn_2S_4 structure. Recently, Donica et al. reported the existence of sixteen kinds of polytypes in ZnIn_2S_4 (9). These polytypes can be distinguished by the difference of the stacking of sulfur atoms. Hexagonal unit cell parameters of these polytypes are $a = 3.85 \text{ \AA}$ and $c = n \times 12.34 \text{ \AA}$, where n is an integer ranging from 1 to 24. This fact suggests that the crystal structures of MnGa_2S_4 I, II, and III may be explained due to such polytypism found in ZnIn_2S_4 . Considering that the ZnIn_2S_4 structure has a vacant layer at every fourth layer, such a stability of ZnIn_2S_4 -like layer structure in MnGa_2S_4 at high pressure is quite striking.

In addition, it is to be noted that neither spinel structure nor decomposition reaction were observed in the complex phase transformations. These results in MnGa_2S_4 are quite contrasted to those of MnAl_2S_4 . Since the values of the ionic radius and the electronegativity of gallium scarcely differ from those of aluminium, the difference between the modes of high pressure transformations in MnGa_2S_4 and MnAl_2S_4 should be sought in the difference in

the chemical nature of Al^{3+} and Ga^{3+} ions. Finally, we would like to point out that crystal structure of most high-pressure phases are still undetermined and much work must be done before we can discuss these problems in detail.

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