

## Homologous Series in the MnS-Y<sub>2</sub>S<sub>3</sub> System

### HOMOLOGOUS SERIES, $x\text{MnS}\cdot\text{Y}_2\text{S}_3$ , WITH $x = 0\text{--}0.5$

Here we are interested in two phases in this system:  $\text{MnS}\cdot\text{Y}_2\text{S}_3 = \text{MnY}_2\text{S}_4$  and  $\text{MnS}\cdot 2\text{Y}_2\text{S}_3 = \text{MnY}_4\text{S}_7$ . A series of structures characteristic of a TCT mechanism is formed based on these two structures (Bakker and Hyde, 1978) in a way which is similar to the case of *phase V* in the  $\text{PbS}\text{-Bi}_2\text{S}_3$  system. Accordingly, an account of their structures is given first.

The former (Patrie and Chevalier, 1966; Flahaut *et al.*, 1961) is isostructural with  $\text{CaTi}_2\text{O}_4$  (Bertaut and Blum, 1956); both are isotypic to the orthorhombic structure of hypothetical lillianite homologue  $\text{PbBi}_2\text{S}_4$ , (4,4). Their cell dimensions are compared below:

$$\text{CaTi}_2\text{O}_4: a = 9.727 \text{ \AA}, b = 9.976 \text{ \AA}, c = 3.136 \text{ \AA},$$

$$\text{MnY}_2\text{S}_4: a = 12.62 \text{ \AA}, b = 12.75 \text{ \AA}, c = 3.78 \text{ \AA}^*,$$

$$\text{PbBi}_2\text{S}_4: a = 13.92 \text{ \AA}, b = 14.30 \text{ \AA}, c = 4.20 \text{ \AA}.$$

They have space group  $Bbmm$  ( $D_{2h}^{17}$ —No. 63) and  $Z = 4$ . The cell dimensions for  $\text{PbBi}_2\text{S}_4$  are those calculated from the cell parameter of  $\text{PbS}$  (Otto and Strunz, 1968). The  $b$  length of this hypothetical structure corresponds to double width ( $2 \times 6.65 \text{ \AA}$ ) of the B slab of *phase V* (Chapter 3). The structure of  $\text{CaTi}_2\text{O}_4$ , which has been well studied, is illustrated in Fig. 1. The cation site locating in the set of mirror planes has di-capped trigonal prismatic coordination and accommodates Ca. This site in  $\text{MnY}_2\text{S}_4$ , that we are now concerned with, should be occupied not by a divalent atom but a trivalent Y, with the remaining Y and Mn most likely statistically distributed over the octahedral positions.

The latter phase  $\text{MnY}_4\text{S}_7$  is isostructural with  $\text{Y}_5\text{S}_7$  (Adolphe, 1965), which is isotypic to V1. The cell dimensions of these two compounds are compared below:

$$\text{Y}_5\text{S}_7: a = 12.768 \text{ \AA}, b = 11.545 \text{ \AA}, c = 3.803 \text{ \AA}, \gamma = 104.82^\circ,$$

$$\text{MnY}_4\text{S}_7: a = 12.636 \text{ \AA}, b = 11.443 \text{ \AA}, c = 3.790 \text{ \AA}, \gamma = 105.45^\circ.$$

The  $b$  and  $c$  axes chosen by Adolphe (1965) are interchanged in the above list in order to discuss them on the same basis of V1,  $\text{PbBi}_4\text{S}_7$ , (Chapter 3). They have space group  $B2/m$  ( $C_{2h}^1$ —No. 10) and  $Z = 2$ . As will be observed in Fig. 2, the structure of  $\text{Y}_5\text{S}_7$  is built up of a contracted twin (4,3) as in the case of V1. The cations at M(2), near the contact plane, is, however, more symmetrical in comparison to the case of V1 and has a trigonal prismatic coordination (mean Y-S distance of  $2.82 \text{ \AA}$ ) with an additional sulfur atom, S1, at a distance  $2.96 \text{ \AA}$ . This trigonal prism is hence mono-capped; the third near sulfur atom, S2, is at much longer distance of  $3.81 \text{ \AA}$ . The mean bond lengths for M(1) and M(3) octahedra are  $2.71 \text{ \AA}$  and  $2.72 \text{ \AA}$ , respectively.

In the structure of  $\text{MnY}_4\text{S}_7$ , the site corresponding to M(2) will most probably

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\*After Patrie and Chevalier (1966).

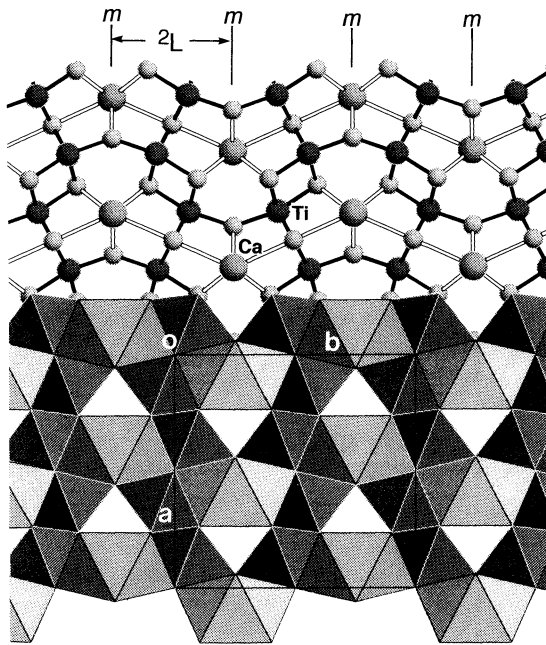


Fig. 1. The  $c$ -axis projection of the structure of  $\text{CaTi}_2\text{O}_4$ . Large spheres denote Ca, dark medium spheres Ti and small spheres oxygen atoms. The Ti-O bonds are indicated by filled lines.

be occupied by Y and the octahedral sites by Mn and the remaining Y.

Now, the series of structures observed by Bakker and Hyde (1978) by means of electron microscopy are listed in Table 1. Although long-range ordering tends to be imperfect, they confirmed the existence of at least one ordered phase  $\text{Mn}_2\text{Y}_6\text{S}_{11}$ , which is isotypic to V2, in addition to the two phases discussed above.

Among other structures they observed, some are interrupted by mistake and some by intergrowth of others. One of the features of this structure series lies, as argued, in the distribution of yttrium atoms at the cation sites in the contact planes of both the cell-twinning and contracted twinning. This situation immediately suggests that the smaller the mean width,  $\bar{n}$ , of the cell-twin unit, the greater the yttrium content. In Table 1, we find that the TCT mechanism in this chemical series exactly goes along this line. Note that the last four structure types have been found for *phase V* in the  $\text{PbS-Bi}_2\text{S}_3$  system; the relationship between chemical composition and structure of the  $\text{MnY}_2\text{S}_4\text{-MnY}_4\text{S}_7$  series can be studied in a way which is similar to the case of *phase V*.

However, it is notable that Bakker and Hyde (1978) observed the existence of two new structure types (Table 1) which have not been found in the *phase V* subseries. Bearing in mind that the symbols 4 and 3 correspond to B ( $=^2L$ ) and A ( $=^1L$ ), respectively, these two structures are rewritten in terms of A and B as follows:

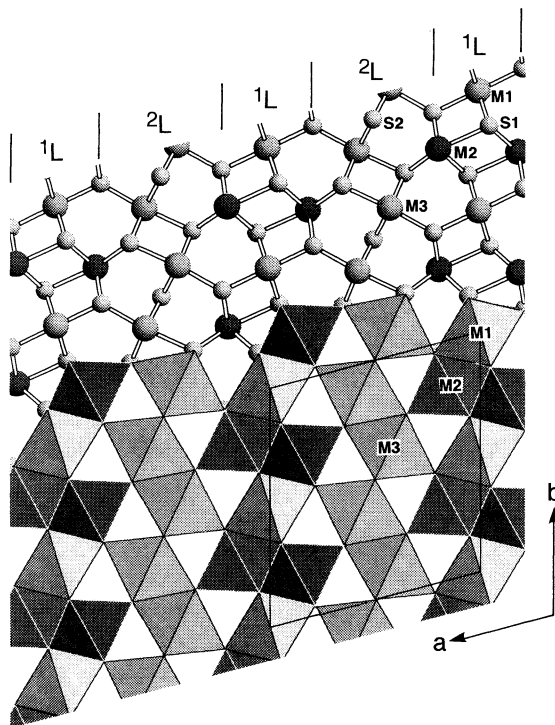


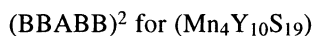
Fig. 2. The *c*-axis (3.8 Å axis) projection of the structure of Y<sub>5</sub>S<sub>7</sub>.

Table 1. Homologous series in the MnS-Y<sub>2</sub>S<sub>3</sub> system

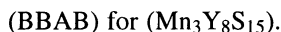
Mole ratio MnS/Y <sub>2</sub> S <sub>3</sub>	Chemical composition	Cell-twin type	$\bar{n}$	$d_{(010)}$ *	Probable space group
1/1	MnY <sub>2</sub> S <sub>4</sub>	(4) <sup>2</sup>	4	12.8 Å	Bbmm
4/5	Mn <sub>4</sub> Y <sub>10</sub> S <sub>19</sub>	(4, 4, 3, 4, 4) <sup>2</sup>	3.80	60	Bbmm
3/4	Mn <sub>3</sub> Y <sub>8</sub> S <sub>15</sub>	(4, 4, 3, 4)	3.75	24	B2/m
2/3	Mn <sub>2</sub> Y <sub>6</sub> S <sub>11</sub>	(4, 3, 4) <sup>2</sup>	3.67	35	Bbmm
3/5	Mn <sub>3</sub> Y <sub>10</sub> S <sub>18</sub>	(4, 3, 4, 3, 4) <sup>2</sup>	3.60	57	Bbmm
4/7	Mn <sub>4</sub> Y <sub>14</sub> S <sub>25</sub>	(4, 3, 4, 3, 4, 3, 4) <sup>2</sup>	3.57	79	Bbmm
1/2	MnY <sub>4</sub> S <sub>7</sub>	(4, 3)	3.50	11.0	B2/m

The same set of axes is used as for *phase V* in the PbS-Bi<sub>2</sub>S<sub>3</sub> system.

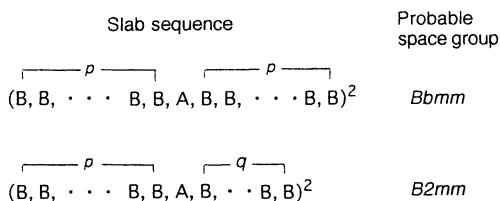
\*Rounded off version of the calculated values given by Bakker and Hyde (1978).



and



The discovery of those structures advances us toward prediction of the two new series of orthorhombic structures shown below: In this diagram, the letters  $p$  and  $q$  stand for  $p$ -fold succession of B slabs and  $q$ -fold succession of B slabs, respectively, where  $p$  and  $q$  are integers and  $p \neq q$ .



There are quite a few compounds which are isostructural with  $\text{MnY}_2\text{S}_4$  or  $\text{MnY}_4\text{S}_7$ , i.e.  $\text{MnYb}_2\text{S}_4$ ,  $\text{MnDy}_2\text{S}_4$ ,  $\text{MnHo}_2\text{S}_4$ ,  $\text{FeYb}_2\text{S}_4$  etc. (Patrie and Chevalier, 1966), or  $\text{MnYb}_4\text{S}_7$ ,  $\text{MnDy}_4\text{S}_7$ ,  $\text{FeYb}_4\text{S}_7$  etc. (Adolphe, 1965), respectively. We may then expect that further examples of chemical series like the present case will be found for the chemical systems in which these phases are involved.

#### REFERENCE

- Adolphe, C.: Contribution a l'étude d'un groupe de sulfures isostructuraux de terres rares et d'yttrium de type:  $\text{Y}_5\text{S}_7$  et  $\text{FeY}_4\text{S}_7$ . *Ann. Chim.* **10** (1965) 271–297.
- Bakker, M. and Hyde, B. G. (1978): vid. Chapter 3.
- Bertaut, E. F. and Blum, P.: Détermination de la structure de  $\text{Ti}_2\text{CaO}_4$  par la méthode self-consistente d'approche directe. *Acta Cryst.* **9** (1956) 121–126.
- Flahaut, J., Domange, L., and Patrie, M.: Combinaisons formées par sulfures des éléments du group des terres rares. III.—Les systèmes sulfure d'yttrium-sulfure de magnésium, et sulfure d'yttrium-sulfure de manganèse. *Bull. Soc. Chim. Fr.* (1961) 1887–1891.
- Otto, H. H. and Strunz, H. (1968): vid. Chapter 3.
- Patrie, M. and Chevalier, M. R.: Sur une famille de composés orthorhombiques du type  $\text{MnY}_2\text{S}_4$ . *C. R. Acad. Sc. Paris, Serie C* **263** (1966) 1061–1064.