CHEMISTRY LETTERS, pp. 2057-2060, 1990.

Preparation, Characterization, and Intercalation of $(PbS)(TS_2)_2$;(T = Ti, Nb, Ta), New Ternary Sulfides with Layered Composite Crystal Structure

Yoshito GOTOH, Junji AKIMOTO, Makoto SAKURAI, Yoshimichi KIYOZUMI,
Kunio SUZUKI, and Yoshinao OOSAWA
National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305

A few $(PbS)(TS_2)_2$;(T = Ti, Nb, Ta) type of ternary sulfides has been prepared. On the basis of powder X-ray diffraction, it is suggested that they have layered composite crystal structure in which a two-atom-thick PbS layer and two adjacent three-atom-thick TS_2 sandwiches are stacked alternately. Intercalation of hydrazine into the sulfides has been observed.

Recently many ternary sulfides with layered composite crystal structure have been reported: $(MS)_nTS_2$(M = Lanthanides, Pb, Sn, Bi; T = Ti, V, Nb, Ta, Cr; n = 1.08-1.19).[1,2] In these compounds, two-atom-thick MS layer with distorted NaCl structure and three-atom-thick TS_2 sandwich with T in octahedral or trigonal prismatic coordination are stacked alternately. It is known that the binary sulfide(MS or TS_2) which constitutes $(MS)_nTS_2$ is superconductor, host compounds for intercalation, semiconductor sensor for near-infrared light, and so on. Therefore these ternary sulfides are interesting from the standpoint of not only structure, but also physical properties and functions.

In addition to the $(MS)_nTS_2$ type of sulfides, sulfides with MT_2S_5 formula have been reported. They are $PbNb_2S_5$, $SnTi_2S_5$,[3] and BiT_2S_5(T =

Ti, Nb, Ta).[4)] We have found that BiT_2S_5(T = Ti, Nb, Ta) seems to have layered composite crystal structure similar to that of $(MS)_nTS_2$ type of sulfides and consist of a two-atom-thick MS layer and two adjacent three-atom-thick TS_2 sandwiches alternately stacked.[4)] Therefore it seems more adequate to represent the BiT_2S_5 type of sulfides as $(BiS)_n(TS_2)_2$. We also have found that intercalation of hydrazine occurs in $(BiS)_n(TS_2)_2$ which shows that the interface of two adjacent TS_2 sandwiches has the character of van der Waals plane like corresponding binary TS_2. In the present manuscript, we preliminarily report preparation, and characterization of $(PbS)(TiS_2)_2$ and $(PbS)(TaS_2)_2$. Intercalation of hydrazine into $(PbS)(TS_2)_2$(T = Ti, Nb, Ta) is also reported.

These sulfides were prepared as follows. Starting materials(powder of Pb(purity 3N), Ti(3N), Nb(3N6), Ta(3N6), S(4N)) were mixed together in the ratio of Pb/T/S = 1/2/5 and sealed in a silica tube. The tube was heated at first at 500 °C and then at 800 °C. X-Ray powder diffraction was measured using counter-diffractometer method.

The X-ray diffraction patterns of $(PbS)(TiS_2)_2$ and $(PbS)(TaS_2)_2$ consist of several strong peaks and a few medium and weak peaks. The strong peaks are attributable to a set of parallel planes $(0\ 0\ \ell)$ as in the case of $(BiS)(TS_2)_2$. This fact suggest that the compounds have some layered structure and take preferred orientation. Because the X-ray diffraction lines other than $(0\ 0\ \ell)$ are rather weak and broad probably owing to the preferred orientation and stacking disorder, we here show only the $(0\ 0\ \ell)$ diffraction data in Table 1.

According to single crystal X-ray structure determination of $(PbS)_{1.12}VS_2$,[5,6)] $(PbS)_{1.14}NbS_2$,[7)] $(PbS)_{1.13}TaS_2$,[8)] their structure in the layer-stacking direction consists of a two-atom-thick MS layer with distorted NaCl structure and a three-atom-thick TS_2 sandwich with T in octahedral or trigonal prismatic coordination, and the length of the structure in the layer-stacking direction is around 12 Å.

On the other hand, the periodic length of the present $(PbS)(TS_2)_2$ type

Table 1. X-Ray powder diffraction data of $(0\ 0\ l)$ diffraction lines of $(PbS)(TiS_2)_2$ and $(PbS)(TaS_2)_2$

h	k	l	d_{calcd}/Å	d_{obsd}/Å	$(I/I_0)_{obsd}$	d_{calcd}/Å	d_{obsd}/Å	$(I/I_0)obsd$
				$(PbS)(TiS_2)_2$			$(PbS)(TaS_2)_2$	
0	0	n	17.45	17.9	5	——	——	—
0	0	2n	8.724	8.75	3	9.000	9.00	4
0	0	3n	5.816	5.817	23	5.999	6.022	100
0	0	4n	4.362	4.360	38	4.500	4.497	29
0	0	5n	3.489	3.481	58	3.600	3.601	27
0	0	6n	2.908	2.919	100	——	——	—
0	0	7n	2.492	2.490	24	2.571	2.569	16
0	0	8n	2.181	2.182	16	2.250	2.251	5
0	0	9n	1.939	1.939	16	2.000	2.000	23
0	0	10n	——	——	—	——	——	—
0	0	11n	——	——	—	——	——	—
0	0	12n	1.4539	1.4525	35	1.4998	1.5001	20

of sulfides is in the range of 17.5-18.0 Å. The length becomes larger with an increase in the atomic radius of the constituent T element. Table 2 represents the periodic lengths of $(PbS)_nTS_2$ and $(PbS)(TS_2)_2$ and their difference for given T. Each difference coincides well with the periodic length of the corresponding disulfides in the layer-stacking direction. Therefore these $(PbS)(TS_2)_2$ type of sulfides seem to be represented by a model depicted in Fig. 1: a two-atom-thick layer of PbS and two adjacent three-atom-thick sandwiches of TS_2 are stacked alternately as in the case of $(BiS)(TS_2)_2$.

It is expected that some electron-donating guest molecule or ions can intercalate into the interface between the two adjacent TS_2 layers as in the case of the $(BiS)(TS_2)_2$. In fact, the periodic length of $(PbS)(TS_2)_2$ in the layer-stacking direction became larger when the sulfide was soaked in hydrazine hydrate at room temperature. The length of enlargement is around 3 Å for every $(PbS)(TS_2)_2$. On the other hand, no intercalation occured when $(PbS)_nTS_2$ was soaked in hydrazine hydrate. This fact means that hydrazine does not intercalate into the interface between PbS and TS_2

layers. Therefore it is suggested that hydrazine(probably in the form of hydrazinium ion) is intercalated into the interface between the two adjacent TS_2 layers.

Table 2. Periodic lengths(Å) of $(PbS)_nTS_2$ and $(PbS)(TS_2)_2$, and their difference

T	Ti	Nb	Ta
$(PbS)_nTS_2$	11.78[a]	11.90[b]	11.98[c]
$(PbS)(TS_2)_2$[d]	17.45	17.86[e]	18.00
Difference	5.67	5.96	6.02
TS_2	5.66[f]	5.97[g]	6.01[f]

a) Our data obtained with powder sample.
b) Ref. 7.
c) Ref. 8.
d) Value calculated from (0 0 n) diffraction line in Table 1.
e) 17.92 A is obtained from Ref.3.
f) JCPDS No.: TiS_2, 36-1406; TaS_2, 2-137
g) D. R. Powell and R. A. Jacobson, J. Solid State Chem., 37, 140(1981).

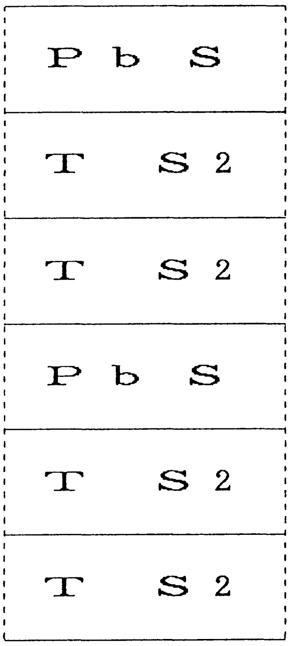

Fig. 1. Schematic drawing of $(PbS)_n(TS_2)_2$.

References

1) G. A. Wiegers, A. Meetsma, R. J. Haange, and J. L. de Boer, Solid State Ionics, 32, 183(1989).
2) G. A. Wiegers et al., Solid State Commun., 70, 409(1989).
3) L. Guemas, P. Rabu, A. Meerschaut, and J. Rouxel, Mat. Res. Bull., 23, 1061(1988).
4) Y. Oosawa, Y. Gotoh, and M. Onoda., Chem. Lett., 1989, 1563.
5) Y. Gotoh, M. Goto, K. Kawaguchi, Y. Oosawa, and M. Onoda, Mat. Res. Bull., 25, 307(1990).
6) M. Onoda, K. Kato, Y. Gotoh, and Y. Oosawa, Acta Crystallogr., Sect. B, 46, 487(1990).
7) G. A. Wiegers, A. Meetsma, R. J. Haange, S. van Smaalen, and J. L. de Boer, Acta Crystallogr., Sect. B, 46, 324(1990).
8) J. Wulff, A. Meetsma, S. van Smaalen, R. J. Haange, J. L. de Boer, and G. A. Wiegers, J. Solid State Chem., 84, 118(1990).

(Received August 16, 1990)