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Preparation and Characterization of BiM_2X_5 (M = Ti, Nb, Ta; X = S, Se), New Composite-Layered Chalcogenides[1)]

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A few BiM_2X_5-type of chalcogenides($BiTi_2S_5$, $BiNb_2S_5$, $BiTa_2S_5$, $BiNb_2Se_5$) have been prepared from the elements. On the basis of powder X-ray diffraction, it is suggested that they have composite-layered structure in which a BiX layer and two adjacent BX_2 layers are stacked alternately. Intercalation of hydrazine into BiM_2X_5 has been observed.

Recently much attention has been paid for composite-layered chalcogenides with AMX_3 formula. Three series of the chalcogenides have been reported: $LnMS_3$(Ln = Lanthanides, M = Cr, Nb, etc.),[2-4)] AMS_3(A = Pb, Sn; B = Ti, V, Nb, Ta),[5-9)] $BiMX_3$(M = Ti, V, Nb, Ta; X = S, Se).[10,11)] In these compounds, layers of AX and MX_2 are stacked alternately. The binary chalcogenides(AX or MX_2) forming AMX_3 are known as superconductor, host compound for intercalation, semiconductor for optical use and so on. Therefore these composite-layered chalcogenides are interesting from the standpoint of not only structure, but also physical properties and functions.

Chalcogenides with AM_2S_5 formula($PbNb_2S_5$ and $SnTi_2S_5$)[5)] which have been reported very recently seem to have a composite-layered structure similar to that of the ABX_3-type of chalcogenides. In the present manuscript, we preliminarily report preparation and characterization of BiM_2X_5-type of chalcogenides: $BiTi_2S_5$, $BiNb_2S_5$, $BiTa_2S_5$, and $BiNb_2Se_5$. Intercalation of hydrazine into BiM_2X_5 is also reported.

These chalcogenides were prepared as follows. Starting materials(powder of Bi(purity 3N), Ti(3N), Nb(3N6), Ta(3N6), S(4N), Se(3N)) were mixed together stoichiometrically and sealed in a silica tube in vacuum. Heat treatment and characterization are similar to those reported in our previous papers.10,11)

The X-ray diffraction pattern consists of several strong peaks and a few weak peaks. The strong peaks are attributable to a set of parallel planes(0 0 ℓ) as in the case of the ABX_3-type of chalcogenides. This fact suggests that the compounds have some layered structures and take preferred orientation. It has been reported that stacking disorder in the ab-plane occurs in these kinds of chalcogenides.8) Since the X-ray diffraction lines other than (0 0 ℓ) are rather weak and broad possibly because of the stacking disorder, we here describe only the (0 0 ℓ) diffraction data. Table 1 shows the X-ray powder diffraction data of (0 0 ℓ) diffraction lines.

Table 1. X-Ray powder diffraction data of (0 0 ℓ) diffraction lines for BiM_2X_5

h	k	l	d_{calcd}/Å	d_{obsd}/Å	$(I/I_0)_{obsd}$	d_{calcd}/Å	d_{obsd}/Å	$(I/I_0)_{obsd}$
				$BiTi_2S_5$			$BiNb_2S_5$	
(0	0	n)	16.99	17.03	37	17.44	—	—
(0	0	2n)	8.496	8.52	3	8.719	—	—
(0	0	3n)	5.664	5.659	32	5.813	5.810	100
(0	0	4n)	4.248	4.248	34	4.356	4.360	52
(0	0	5n)	3.398	3.396	44	3.488	3.486	86
(0	0	6n)	2.832	2.829	100	2.906	2.905	27
(0	0	7n)	2.427	2.425	16	2.491	2.492	24
(0	0	8n)	2.124	2.123	3	2.180	2.182	10
(0	0	9n)	1.888	1.887	4	1.938	1.937	18
(0	0	10n)	1.6991	—	—	1.7438	—	—
(0	0	11n)	1.5446	—	—	1.5853	—	—
(0	0	12n)	1.4159	1.4148	16	1.4532	1.4535	17
				$BiTa_2S_5$			$BiNb_2Se_5$	
(0	0	n)	17.51	—	—	18.33	—	—
(0	0	2n)	8.757	8.75	10	9.163	—	—
(0	0	3n)	5.838	5.84	100	6.109	6.11	40
(0	0	4n)	4.378	4.377	27	4.582	4.582	13
(0	0	5n)	3.503	3.504	37	3.665	3.669	19
(0	0	6n)	2.919	—	—	3.054	3.054	100
(0	0	7n)	2.502	2.502	12	2.618	2.619	26
(0	0	8n)	2.189	2.189	8	2.291	2.291	21
(0	0	9n)	1.946	1.946	10	2.036	2.036	20
(0	0	10n)	1.7513	—	—	1.8326	—	—
(0	0	11n)	1.5921	—	—	1.6660	1.665	3
(0	0	12n)	1.4594	1.4605	9	1.5272	1.5255	44

According to single crystal X-ray structure determination of $LaCrS_3$,[2] $LaNbS_3$,[4] and $SnNbS_3$,[6,7] the periodic structure of the AMX_3-type of chalcogenides in the layer-stacking direction consists of a two-atom-thick AX layer and a three-atom-thick MX_2 layer and the length of the structure in the stacking direction is in the range of 11-12 Å. By considering the similarity between the AMS_3-type of sulfide described above and the $BiMX_3$ in X-ray diffraction pattern and electron diffraction pattern, it has been suggested that the layer-stacking sequence of $BiMX_3$ is represented by a model shown in Fig. 1 (a): a two-atom-thick layer of BiX and a three-atom-thick sandwich of MX_2, X-M-X, are stacked alternately.[10,11] The periodic length in the layer-stacking direction is in the range of 11-12 Å as in the case of the other AMX_3- type of composite-layered compounds.

On the other hand, the periodic length of the present BiM_2X_5-type of chalcogenides is in the range of 17-18 Å as shown in Table 1. The length becomes larger with an increase in the atomic radius of the constituent elements. Table 2 represents the periodic lengths of BiM_2X_5 and $BiMX_3$ and their differences for a given combination of M and X. Each difference coincides well with the periodic length of the corresponding dichalcogenides in the layer-stacking direction. Therefore these BiM_2X_5-type of chalcogenides seem to be represented by a model depicted in Fig. 1 (b): a two-atom-thick layer of BiX and two adjacent three-atom-thick sandwiches of MX_2 are stacked alternately.

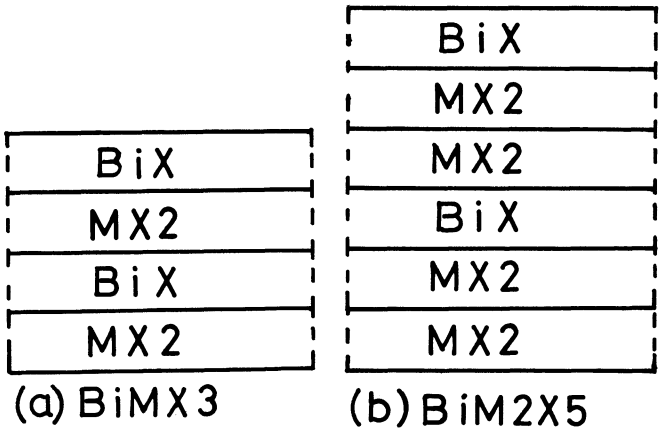

Fig. 1. Schematic drawing of $BiMX_3$ and BiM_2X_5 types of chalcogenide.

It is expected that some guest molecules or ions can intercalate into the interface between the two adjacent MX_2 layers as in the case of the dichalcogenides. In fact, the periodic length of $BiTa_2S_5$ in the layer-stacking direction became larger(to ca. 20.7 Å) when the chalcogenide was soaked in aqueous hydrazine solution at room temperature. The length of enlargement(3.2 Å) is close to that when hydrazine is intercalated into the Van der Waals plane of TaS_2(3.1 Å).[12] On the other hand, no intercalation occurred when $BiTaS_3$ was soaked in

Table 2. Periodic length(Å) of $BiMX_3$, BiM_2X_5, and their difference

	Bi-Ti-S	Bi-Nb-S	Bi-Ta-S	Bi-Nb-Se
$BiMX_3$[a)]	11.31	11.51	11.55	12.10
BiM_2X_5[b)]	16.99	17.44	17.51	18.33
Difference Between $BiMX_3$ and BiM_2X_5	5.68	5.93	5.96	6.23
MX_2	5.66[c)]	5.97[d)]	6.01[c)]	6.25[c)]

a) Calculated d value for (0 0 n) diffraction line in Ref. 11.

b) Calculated d value for (0 0 n) diffraction line in Table 1.

c) JCPDS No.: TiS_2, 36-1406; TaS_2, 2-137; $NbSe_2$, 18-923.

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aqueous hydrazine solution. This fact means that hydrazine does not intercalate into the interface between BiS and TaS_2 layers. Therefore in the case of $BiTa_2S_5$, it is suggested that hydrazine is intercalated into the interface between the two adjacent TaS_2 layers. Intercalation of hydrazine was also observed for the other BiM_2X_5-type of chalcogenides, and for $PbNb_2S_5$ and $SnTi_2S_5$.

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