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Preparation and Characterization of $BiMX_3$ (M = Ti, V, Nb, Ta; X = S, Se), New Composite-Layered Chalcogenides[1)]

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The title chalcogenides have been prepared from the elements. On the basis of powder X-ray diffraction and electron diffraction studies, it is suggested that they have a composite-layered structure in which layers of BiX and MX_2 are stacked alternately. The periodic length of $BiMX_3$ in the layer-stacking direction increases with an increase in the atomic radius of M and X.

Two series of composite-layered sulfides of general formula AMS_3 are known; in one series, A is lanthanides,[2-4)] and in the other Pb[5,6)] or Sn.[5,7-9)] In these sulfides layeres of AS and MS_2 are stacked alternately. Recently these types of sulfides have begun to arouse much interest in the study on their novel structures. We have found the third series of composite-layered chalcogenides of the formula AMX_3(A = Bi, Sb; M = Ti, V, Nb, Ta; X = S, Se). Among them $BiTaS_3$ has been described already in our preceding paper.[10)] In the present manuscript $BiMX_3$ except for $BiTaS_3$ will be preliminarily reported.

$BiMX_3$ was prepared in a manner similar to that reported in the preceding paper.[10)] Starting materials(powder of Bi(purity, 3N), Ti(3N), V(2N), Nb(3N6), Ta(3N6), S(4N), and Se(3N)) were mixed stoichiometrically and sealed in a silica tube in vacuum. After heat treatment at 500 °C and 800 °C, the chalcogenides were obtained as black-grayish microcrystalline powder with luster. The X-ray diffraction patterns were taken by the counter-diffractometer technique by using

Ni-filtered CuKα_1 radiation. The electron diffraction patterns were taken from the crushed particles by a 100 kV electron microscope.

All the X-ray diffraction patterns of $BiMX_3$ resemble that of $BiTaS_3$ and consist of several strong peaks and a few weak peaks. The strong peaks are attributable to a set of parallel planes (0 0 ℓ). Figure 1 shows the electron diffraction pattern of $BiVS_3$ with an incident beam parallel to the [0 0 1] direction. The pattern can be analyzed on the basis of a composite crystal like $LaCrS_3$[3] or $SnNbS_3$.[5,7,8] That is to say, the diffraction pattern can be interpreted as superposition of a pseudo-tetragonal subcell of Bi and S and a pseudo-hexagonal subcell of V and S as in the case of $BiTaS_3$. We adopt orthohexagonal axes $\mathbf{a}^*_{OH}$ and $\mathbf{b}^*_{OH}$ for a pseudo-hexagonal subcell. The two subcells have the same periodicity in $\mathbf{a}^*$ axis: $a^*_T = a^*_{OH}$. However they have different periodicity in $\mathbf{b}^*$ axis and are in nearly commensurate relation of $b^*_T/12 = b^*_{OH}/11$.

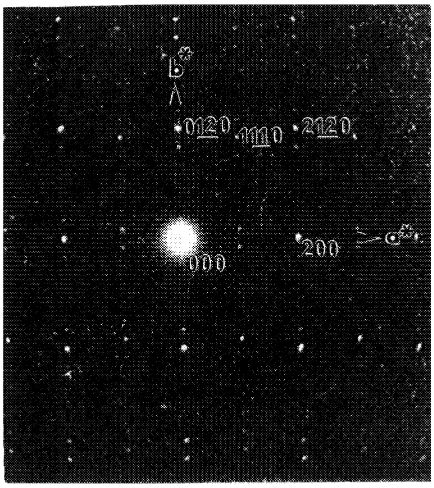

Fig. 1. The electron diffraction pattern of $BiVS_3$ with an incident beam along the [0 0 1] direction.

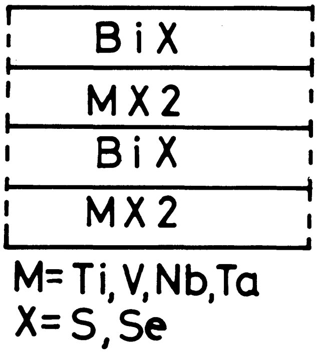

Fig. 2. A layer-stacking model of $BiMX_3$.

The similarity of X-ray diffraction patterns for all the other chalcogenides of the formula $BiMX_3$ described above suggests that they all have similar structures. According to the structure determination of $LaCrS_3$,[2] $LaNbS_3$,[4] and $SnNbS_3$,[7,8] it is suggested that the layer-stacking sequence of $BiMX_3$ is represented by a model shown in Fig. 2: two-atom-thick layer of BiX and three-atom-thick sandwiches of MX_2 are stacked alternately. It has been reported that stacking disorder in the ab-plane occurs in these kinds of chalcogenides.[9] Since the X-ray diffraction lines other than (0 0 ℓ) are rather weak and broad possibly because of the

Table 1. X-Ray powder diffraction data of (0 0 ℓ) lines for $BiMX_3$

h	k	l	d_{calcd}/Å	d_{obsd}/Å	$(I/I_0)_{obsd}$	d_{calcd}/Å	d_{obsd}/Å	$(I/I_0)_{obsd}$
				$BiTiS_3$			$BiVS_3$	
(0	0	n)	11.31	11.31	48	11.27	11.25	30
(0	0	2n)	5.654	5.65	19	5.636	5.63	7
(0	0	3n)	3.769	3.767	90	3.757	3.759	100
(0	0	4n)	2.827	2.825	100	2.818	2.820	70
(0	0	5n)	2.262	2.262	17	2.254	2.256	7
(0	0	6n)	1.885	1.885	3	1.879	1.881	6
(0	0	7n)	1.6154	1.617	<1	1.6103	1.608	<1
(0	0	8n)	1.4135	1.4139	7	1.4088	1.4105	3
				$BiNbS_3$			$BiTaS_3$[10)]	
(0	0	n)	11.51	11.55	4	11.56	11.55	8
(0	0	2n)	5.756	5.76	21	5.779	5.77	59
(0	0	3n)	3.837	3.839	100	3.853	3.849	100
(0	0	4n)	2.878	2.878	45	2.890	2.890	13
(0	0	5n)	2.302	2.301	18	2.312	2.311	30
(0	0	6n)	1.919	1.918	9	1.926	1.928	10
(0	0	7n)	1.6444	1.6394	<1	1.6511	1.6516	<1
(0	0	8n)	1.4389	1.4379	9	1.4447	1.4446	12
				$BiTiSe_3$			$BiVSe_3$	
(0	0	n)	11.84	11.83	12	11.92	11.98	7
(0	0	2n)	5.919	5.92	11	5.960	5.965	11
(0	0	3n)	3.946	3.948	15	3.973	3.971	20
(0	0	4n)	2.960	2.960	100	2.980	2.974	100
(0	0	5n)	2.368	2.369	9	2.384	2.382	7
(0	0	6n)	1.973	1.971	3	1.987	—	—
(0	0	7n)	1.6910	—	—	1.7029	—	—
(0	0	8n)	1.4798	1.4798	10	1.4900	1.486	8
				$BiNbSe_3$			$BiTaSe_3$	
(0	0	n)	12.100	12.08	1	12.166	12.19	13
(0	0	2n)	6.050	6.05	27	6.083	6.075	100
(0	0	3n)	4.033	4.033	30	4.055	4.049	93
(0	0	4n)	3.025	3.023	100	3.042	3.041	81
(0	0	5n)	2.420	2.421	27	2.433	2.433	73
(0	0	6n)	2.017	2.019	4	2.028	2.029	10
(0	0	7n)	1.7286	1.730	1	1.7380	1.739	7
(0	0	8n)	1.5125	1.5120	16	1.5208	1.5209	35

stacking disorder, we here describe only the (0 0 ℓ) diffraction lines. In Table 1 are presented X-ray diffraction data of (0 0 ℓ) diffraction lines. For $BiTaS_3$ and $BiVS_3$ n seems to be 2 with the aid of electron diffraction including c^* axis. The fact that n equals 2 means that the periodic structure in the layer-stacking direction consists of 2 sets of BiX(two-atom-thick)-MX_2(three-atom-thick) layers. Similar results have been reported for $PbNbS_3$5) and $LaNbS_3$.4) The values of n for all the other chalcogenides mentioned above are not yet clear. The d value for (0 0 n) in Table 1 gives the periodic length corresponding to one BiX(two-atom-thick)-MX_2(three-atom-thick) layer unit, which increases with an increase in the atomic radius of M and X.

Table 2. Difference of periodic length(Å) between $BiMX_3$ and MX_2 in the layer-stacking direction

M and X	Ti-S	V-S	Nb-S	Ta-S	Ti-Se	V-Se	Nb-Se	Ta-Se
$BiMX_3$[a)]	11.31	11.25	11.51	11.56	11.84	11.92	12.10	12.17
MX_2	5.66[b)]	5.73[b)]	5.97[c)]	6.01[b)]	6.01[b)]	6.10[d)]	6.25[b)]	6.33[b)]
Difference	5.65	5.52	5.54	5.55	5.83	5.82	5.85	5.84

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

b) JCPDS-No.: TiS_2, 36-1406; VS_2, 36-1139; TaS_2, 2-137; $TiSe_2$, 30-1383; $NbSe_2$, 18-923; $TaSe_2$, 18-1309.

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Table 2 represents the difference of periodic length between $BiMX_3$ and MX_2 in the layer-stacking direction. The difference is almost constant for the sulfides or for the selenides. According to the model depicted in Fig. 2, the values should correspond to the thickness of BiS layer and BiSe layer, respectively.

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