CHEMISTRY LETTERS, pp. 523-524, 1989.

Preparation and Characterization of $BiTaS_3$ a New Layered Ternary Sulfide[1)]

Yoshinao OOSAWA,* Yoshito GOTOH, and Mitsuko ONODA+
National Chemical Laboratory for Industry, Higashi, Tsukuba, Ibaraki 305
+National Institute for Research in Inorganic Materials, Namiki, Tsukuba, Ibaraki 305

$BiTaS_3$, a new layered ternary sulfide, has been prepared from the elements. The X-ray diffraction pattern of the sulfide is indexed on the basis of pseudo-orthorhombic cell with the lattice parameters of $a = 6.10$ Å, $b = 38.3$ Å, and $c = 23.115$ Å.

Layered binary chalcogenides have attracted much attention in both physics and chemistry as superconductor, two-dimensional conductor, host compound of intercalation, and so on. It is expected that layered ternary chalcogenides show more variety in physical properties than binary chalcogenides do, because for the formers the number of constituent elements is larger and there is a possibility that the formation of solid solution becomes easier. As layered ternary chalcogenides, $LaMS_3$(M = Cr, Mn, Fe, Co),[2-4)] $PbMS_3$(M = Ti, Nb, Ta)[5-7)] and so on are known. The number of layered ternary chalcogenide is not so large and their structures or physical properties have not intensively studied yet. Now we wish to report the preparation and characterization of $BiTaS_3$, a new layered ternary sulfide.

$BiTaS_3$ was prepared as follows. Starting materials(powder of Bi(purity, 3N), Ta(3N6), and S(3N) in molar ratio of 1/1/3) were mixed together and sealed in a silica tube in vacuum. The tube was placed in an electric furnace, heated at 500 °C for 12 h, then at 800 °C for 48 h , and cooled to room temperature. Thus the sulfide was obtained as black-grayish microcrystalline powder with luster. The X-ray diffraction pattern was taken by the counter-diffractometer technique using Ni-filtered CuKα radiation. Electron diffraction patterns were taken from the crushed particles using a 100 kV electron microscope.

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 (00ℓ). This fact suggests that the compound has some layered structure and takes preferred orientation. Figure 1 shows the electron diffraction pattern with an incident beam parallel to the [001] direction. The rather complicated pattern can be analyzed on the basis of a composite crystal like $LaCrS_3$[3,4)] consisting of two kinds of sulfide layers piled up alternately. That is to say, the diffraction pattern is to be understood as superposition of a pseudo-tetragonal subcell of Bi and S, and a pseudo-hexagonal subcell of Ta and S. We adopt orthohexagonal axes $\mathbf{a}^*_{OH}$ and $\mathbf{b}^*_{OH}$ for a pseudo-hexagonal subcell. The two subcells have same

periodicity in a^* axis($a^*_T = a^*_{OH}$). But they have different periodicity in b^* axis and are in nearly commensurate relation of $b^*_T/12 = b^*_{OH}/11$. The lattice parameters obtained by assuming pseudo-orthorhombic unit cell based on electron diffraction and X-ray powder diffraction data are as follows: a = 6.10 Å, b = 38.3 Å, c = 23.115 Å. Table 1 illustrates the similarity between the observed and calculated d-spacing values.

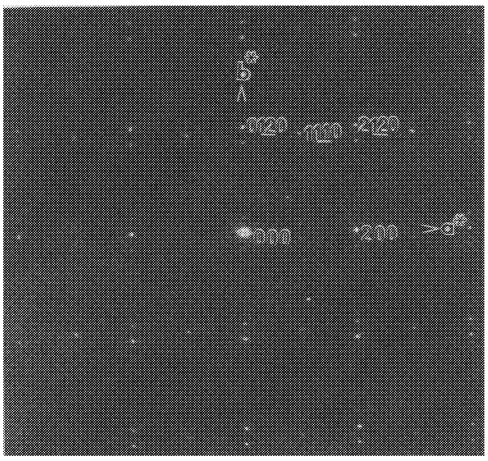

Fig. 1. The electron diffraction pattern with an incident beam along the [001] direction.

Table 1. X-Ray powder diffraction data of $BiTaS_3$

h	k	l	d_{calcd}/Å	d_{obsd}/Å	$(I/I_o)_{obsd}$
0	0	2	11.56	11.55	8
0	0	4	5.779	5.77	59
0	0	6	3.853	3.849	100
2	0	0	3.05	3.036	<1 a)
1	11	0	3.02		<1 a)
0	0	8	2.890	2.890	13
0	0	10	2.312	2.311	30
0	0	12	1.926	1.928	10
				1.799	<1 a)
0	22	3	1.699	1.694	<1 a)
0	0	14	1.6511	1.6516	<1
0	0	16	1.4447	1.4446	12

a) Owing to extreme preferred-orientation, intensity of the diffraction line is very weak and unreliable.

The ideal composition of "$BiTaS_3$" can be analogized according to the reports on $LaCrS_3$ by Kato et al.[3] and Otero-Diaz et al.[4] That is to say, "$BiTaS_3$" would be a composite layered compound consisting of BiS layer and TaS_2 layer. By taking into account the semi-commensurateness in b^* axis found in the electron diffraction pattern, the ideal composition would be expressed as $Bi_{12}Ta_{11}S_{34}$($12BiS + 11TaS_2$). The composition is very close to $BiTaS_3$. The electric conductivity of the compound at 300 K measured by means of d.c. four probe method is 1.6×10^3 S·cm^{-1}.

We have already prepared several compounds with similar structure: ABX_3(A = Bi, Sb; B = Ti, V, Nb, Ta; X = S, Se). Their preparation and characterization including single crystal X-ray structure determination will be reported elsewhere in due course.

We would like to thank Drs. K. Kato and A. Yamamoto of National Institute for Research in Inorganic Materials for their valuable discussions.

References

1) Preparation, Structure, and Properties of Multinary Chalcogenide. Part 1.
2) T. Takahashi, T. Oka, O. Yamada, and K. Ametani, Mater. Res. Bull., 6, 173(1971).
3) K. Kato, I. Kawada, and T. Takahashi, Acta Crystallogr., Sect. B,33, 3437(1977).
4) L. Otero-Diaz, J. D. Fitzgerald, T. B. Williams, and B. G. Hyde, Acta Crystallogr., Sect. B,41, 405(1985).
5) W. Sterzel and J. Horn, Z. Anorg. Allg. Chem., 376, 254(1970).
6) A. V. Novoselova and L. A. Aslanov, Dokl. Akad. Nauk SSSR, 172, 357(1967).
7) L. Guemas, P. Rabu, A. Meerschaut, and J. Rouxel, Mater. Res. Bull., 23, 1061(1988).

(Received December 21, 1988)