Synthetic Phases in the PbS-Bi_2S_3 System; $PbBi_4S_7$ and $Pb_2Bi_2S_5$

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Asahiko SUGAKI*, Hiromi SHIMA* and Arashi KITAKAZE*

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1. Introduction

During the experimental study on the pseudo-binary system of PbS–Bi_2S_3, two synthetic phases were synthesized in addition to heyrovskyite, lillianite and galenobismutite reported in the previous paper[1]. They are $PbBi_4S_7$ and $Pb_2Bi_2S_5$. The synthesis of these phases was performed by a solid reaction between lead and bismuth sulfides. Lead and bismuth sulfides had been synthesized in advance from lead and bismuth metals which are both 99.9+% in purity and sulfur 99.98% in purity.

On the synthetic phases, their synthetic method, optical properties, X-ray powder and crystal data and differential thermal analysis will be described as below in this paper.

2. $PbBi_4S_7$

The synthetic phase with a ideal chemical composition of $PbBi_4S_7$ was identical with Phase V reported by Craig (1967)[2], Otto and Strunz (1968)[3], Salanci and Moh (1969)[4]. From the result of the present experiment, this phase is only stable at high temperatures within its range from 675°C to 735°C and formed a solid solution in compositional range between $Pb_{1.07}Bi_{3.96}S_7$ and $Pb_{0.91}Bi_{4.06}S_7$ at 700°C. This synthetic phase $PbBi_4S_7$ has the same composition as bonchevite ($PbBi_4S_7$), but is not accord with it on X-ray powder data. No mineral which has the composition of $PbBi_4S_7$ has been found in nature up to date.

$PbBi_4S_7$ was synthesized by a solid reaction of lead and bismuth sulfides. Both two sulfides were acculately weighed in the molecular ratio of 7 to 13 to make the composition $Pb_{1.07}Bi_{3.96}S_7$ being included in the solid solution range. They were mixed in an agate mortar under acetone. The mixture was sealed in an evacuated silica glass tube and heated in an electric furnace at 700°C for 7 days. Generally, homogeneous products were obtained by the first heating. After the heating, the products were taken out and ground under acetone. It was again sealed in the evacuated silica glass tube and heated at 730°C for 7 days. After the second heating, it was quenched in cold water. The products were fully sintered aggregate of tabular crystals and megascopicaly lead gray in color with metallic luster.

Under the ore microscope, the synthetic $Pb_{1.07}Bi_{3.96}S_7$ has a weak pleochroism changing its color from white to grayish white in air, and shows a strong anisotropism

* Department of Mining and Mineral Engineering

Table 1. The data of X-ray powder diffraction for synthetic $PbBi_4S_7$.

(1)				(2)		(3)	
I	d(meas.)	hkl	d(calc.)	I	d	I	d
20	6.15	060	6.14	13	5.95	3	5.99
12	4.96	250	4.93	5	4.95	1	4.96
10	3.87	101	3.865	—	—	0.5	3.99
100	3.79	280 121	3.783 3.782	100	3.77	10	3.77
18	3.69	131 0 10 0	3.687 3.684	—	—	—	—
6	3.57	141	3.564	8	3.59	0.5	3.60
8	3.46	290	3.484	—	—	—	—
10	3.43	151	3.422	4	3.42	—	—
25	3.314	400	3.317	13	3.32	1.5	3.31
13	3.278	161	3.271	17	3.30	—	—
3	3.210	430	3.203	4	3.24	—	—
35	2.986	301 311	2.983 2.973	32	2.97	2	2.97
20	2.954	321	2.945				
8	2.908	331	2.899	56	2.91	—	—
4	2.842	341	2.838	5	2.86	—	—
6	2.816	191 470	2.810 2.806	5	2.81	—	—
25	2.773	351	2.765	13	2.77	0.5	2.77
5	2.690	361	2.683	8	2.72	0.5	2.72
3	2.469	4 10 0	2.465	—	—	—	—
18	2.442	2 14 0	2.446	23	2.42	3	2.43
50	2.303	0 16 0	2.302	45	2.30	6	2.30
3	2.233	—	—	14	2.22	1	2.22
3	2.232	—	—	—	—	—	—
15	2.175	531 141	2.183 2.175	10	2.16	1	2.16
7	2.157	541 4 13 0	2.157 2.155	—	—	—	—
7	2.121	551 650	2.124 2.118	6	2.12	0.5	2.12
10	2.086	561	2.086	3	2.08	—	—
7	2.050	571	2.044	3	2.05	—	—
17	2.024	002	2.020	9	2.02	0.5	2.02
18	1.996	581 680	1.998 1.994	9	1.99	1	1.994
10	1.973	—	—	9	1.974	—	—
10	1.968	—	—	10	1.963	1	1.969

(1) Synthetic $Pb_{1.07}Bi_{3.96}S_7$, indicies were calculated by the cell constant as follows; orthorhombic, a=13.27, b=36.84, c=4.04 Å.

(2) Synthetic $PbBi_4S_7$ by Salanci and Moh (1969).

(3) Synthetic $Pb_{1.07}Bi_{3.96}S_7$ by Craig (1967).

with its interference color from dark yellowish gray to dark gray under crossed nicols. When etched by HgCl (20%), it is slowly changed to light brown. By NHO_3 (1: 1), HCl (1: 1), KOH (sat.), $FeCl_3$ (20%) and KCN (30%), it is negative.

The X-ray powder diffraction data of synthetic $Pb_{1.07}Bi_{3.96}S_7$ are shown in Table 1, compared with the data reported by Salanci and Moh (1969)[4] and Craig (1967).[2] Cell constant of the synthetic phase measured by Otto and Strunz (1968)[3] was a following dimension, orthorhombic, $a=13.22\pm0.03$ Å, $b=n\cdot23.30\pm0.02$ Å, $c=4.03\pm0.01$ Å, but n value in b-axis was not mentioned in detail. Recently, Takagi and Takeuchi[5] reported the following three different types of this phase (Phase V); V–1: monoclinic, $a=13.1$, $b=12.0$, $c=4.05$ Å, $\beta=105.2°$, V–2: orthorhombic, $a=13.3$, $b=36.8$, $c=4.03$Å, V–3: $a=13.3$, $b=59.6$, $c=4.03$ Å. Because chemical compositions for these phases were not reported, the relation between cell constant and chemical composition was uncertain.

Cell constant of synthetic phases with chemical composition of $Pb_{1.07}Bi_{3.96}S_7$ and $Pb_{0.87}Bi_{4.08}S_7$ was measured on oscillation, Weissenberg and precession photographs. The schematic diagrams of the reciprocal plane of hk0 for these phases are shown in Fig. 1, A and B. Cell constants of these phases obtained by main reflections in figure was orthorhombic, $a=13.27$, $b=23.13$, $c=4.04$ Å. However, the weak super-

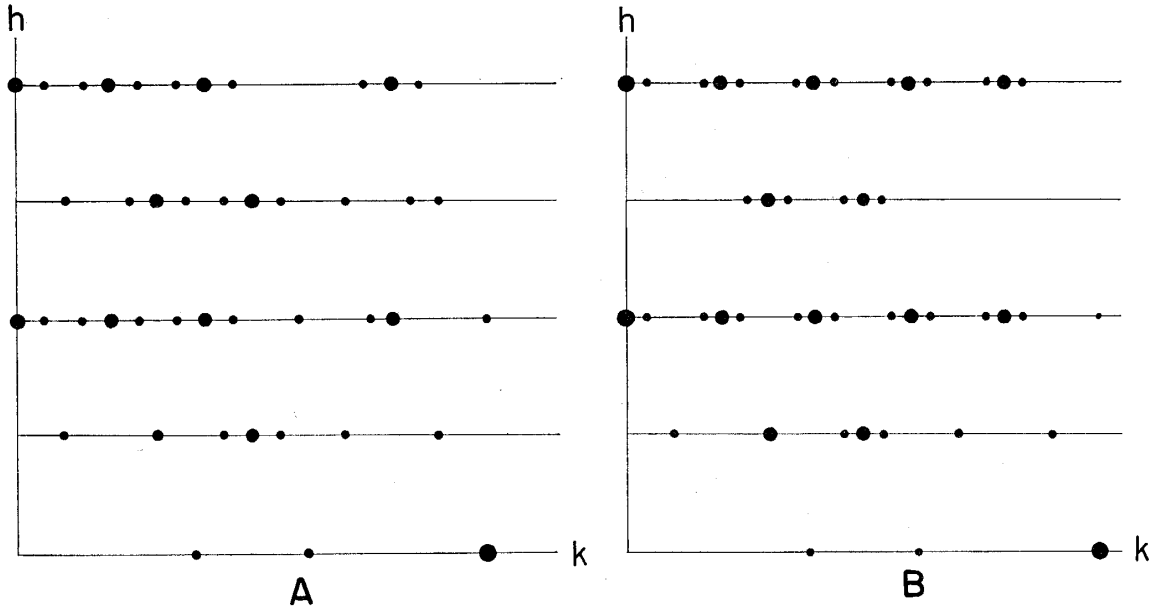

Fig. 1 Schematic diagam of (hk0) plane. A: $Pb_{1.07}Bi_{3.96}S_7$. B: $Pb_{0.87}Bi_{4.08}S_7$.

structure reflections were observed, then these super cells were orthorhombic $a=13.27$, $b=36.8$, $c=4.04$ Å for $Pb_{1.07}Bi_{3.96}S_7$ and $a=13.27$, $b=59.7$, $c=4.04$ Å for $Pb_{0.87}Bi_{4.08}S_7$ respectively. These values are in good agreement with those of the phase V–2 and V–3 reported by Takagi and Takeuchi (1972). The n-values reported by Otto and Strunz[3] for these crystals were 1.59 and 2.58 respectively. From these results, the n-value of b axis was assumed to vary by change of the chemical composition.

The density of synthetic $Pb_{1.07}Bi_{3.96}S_7$ measured by Berman density balance was 6.06 g/cm^2.

Differential thermal analysis curve of synthetic $Pb_{1.07}Bi_{3.96}S_7$ is shown in Fig. 2. A strong endothermic peak beginning at 732°C shows a incongruent melting reaction of this phase to galenobismutite and liquid.

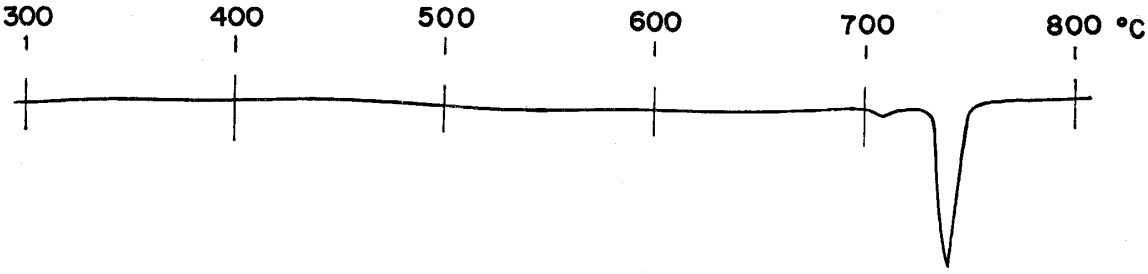

Fig. 2 The differential thermal curve for synthetic $PbBi_4S_7$.

3. $Pb_2Bi_2S_5$ (synthetic new phase)

The synthetic phase $Pb_2Bi_2S_5$ was found as one of the stable phase in the PbS–Bi_2S_3 system during the phase study of this system. This synthetic new phase has a similar chemical composition of cosalite (Pb, Ag, Cu)$_2Bi_2S_5$ which was known well as a lead-bismuth sulfosalt mineral. But these phases were not consistent in their X-ray powder data. While cannizarite has a different composition to $Pb_2Bi_2S_5$, but this synthetic phase has a similar X-ray powder pattern for that reported by Graham et al (1953)[6], Harcout (1942)[7], and Berry and Thompson[8]. The synthetic phase was corresponding to Phase X reported by Salanci and Moh (1968). Both phases have same chemical compositions and similar X-ray powder patterns.

The synthetic phase $Pb_2Bi_2S_5$ was synthesized by solid reaction between lead and bismuth sulfides. Two sulfides were weighed exactly in molecular ratio of two to one, and mixed uniformly under acetone in an agate mortar. The mixture was sealed in the Hario glass tube under vaccum of 10^{-3} mmHg, and put into a regulated electric furnace and heated at 450°C for 5 days. The product was taken out from the glass tube after cooling in air and again mixed under acetone. The mixture sealed in the evacuated glass tube and reheated at 450°C for 15 days and then cooled in air.

The product obtained by reheating become mostly a homogeneous phase, but some times included very slight amount of galenobismutite as impurity. The synthetic phase $Pb_2Bi_2S_5$ is slightly sinterd and megascopically lead gray in color with metallic luster, and has a similar optical properties for other synthetic lead-bismuth sulfosalts under the ore microscope. It shows a weak pleochroism and a strong anisotropism with its interference color from dark gray to yellowish gray under crossed nicols.

The data of X-ray powder diffraction for synthetic phase $Pb_2Bi_2S_5$ as shown in Table 5, shows similar patterns of cannizarite from Lipari Island, Italy reported by Harcout (1942)[7], Graham et al. (1953)[6], and Berry and Thompson (1962)[8].

Table 2. The X-ray powder diffraction data for synthetic $Pb_2Bi_2S_5$

(1)		(2)		(3)		(1)		(2)		(3)	
I	d	I	d	I	d	I	d	I	d	I	d
21	7.64	1	7.38	—	—	7	2.363	0.5	2.39	0.2	2.37
17	5.10	1	5.13	—	—	23	2.232	5	2.22	1.0	2.22
10	4.10	—	—	—	—	10	2.213	—	—	—	—
12	3.94	—	—	—	—	10	2.206	—	—	—	—
100	3.83	10	3.82	3.0	3.80	10	2.184	—	—	—	—
18	3.69	—	—	—	—	18	2.159	—	—	—	—
11	3.60	—	—	—	—	20	2.071	—	—	—	—
63	3.53	3	3.49	1.0	3.51	25	2.065	—	—	—	—
21	3.45	—	—	—	—	35	2.040	5	2.03	3.0	2.03
37	3.42	—	—	—	—	9	2.022	—	—	—	—
44	3.38	3	3.38	1.0	3.35	9	1.982	—	—	—	—
17	3.30	1	3.29	—	—	8	1.970	—	—	—	—
17	3.29					13	1.910	4	1.910	0.5	1.90
14	3.28	—	—	—	—	7	1.893	—	—	—	—
13	3.12	—	—	—	—	9	1.833	—	—	—	—
11	3.07	—	—	—	—	17	1.799	—	—	—	—
42	3.01	6	3.01	3.0	3.00	16	1.797	3	1.791	1.0	1.79
42	3.00					15	1.787	—	—	—	—
36	2.921	—	—	—	—	15	1.778	—	—	—	—
28	2.884	5	2.87	2.0	2.87	5	1.749	—	—	—	—
23	2.783	2	2.76	0.3	2.78	15	1.746	1	1.734	0.5	1.735
17	2.708	—	—	—	—	10	1.728	—	—	—	—
10	2.546	2	2.54	0.2	2.54	10	1.697	—	—	—	—

(1) Synthetic $Pb_2Bi_2S_5$.

(2) Natural cannizarite from Valcano, Lipari Islands, Italy (Berry and Thompson, 1962).

(3) Natural cannizarite from Lipari Islands, Italy (Harcout, 1942).

The stability range of synthetic $Pb_2Bi_2S_5$ was determined by the quenching experiment. It decompose to galenobismutite and lillianite at 500°C, but this reaction is very sluggish and not observed in the differential thermal analysis. Therefor synthetic $Pb_2Bi_2S_5$ was at least stable below the temperature at 500°C.

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