Synthesized Lead Bismuth Sulfosalts Minerals; Heyrovskyite, Lillianite and Galenobismutite

(Synthetic Sulfide Minerals (VI))

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1. Introduction

In order to make clear the stability of sulfide minerals, the experiments on the phase equilibrium relations of several sulfide systems have been carried out by present authors. During the experimental study on the pseudo-binary system of the PbS–Bi_2S_3, sulfosalt minerals such as heyrovskyite, lillianite and gaelnobismutite, and two other synthetic phases were synthesized. The synthetic method, optical properties, X-ray powder and crystal data, and differential thermal analysis of the former three minerals are described here in this paper and those of the synthetic phases will be reported in the next paper of the series. Because the synthetic method of sulfide minerals has been already reported in detail in the previous papers by the present authors[1)2,3,4.5)], it will be mentioned briefly. The synthesis of these sulfosalt minerals were performed by solid reactions between lead and bismuth sulfides which have been synthesized in advance from metallic lead, bismuth and granular sulfur. Lead and bismuth were both 99.9+% in purity and sulfur refined as a guaranteed reagent of 99.98% in purity by Kanto Chemical Co. was used.

2. $Pb_{5.43}Bi_{2.38}S_9$ (Heyrovskyite)

Heyrovskyite is a lead bismuth sulfosalt mineral which has been found recently by Klominsky et al.[6)] (1971) from quartz vein in the Cista granodiorite mass in western Bohemia. They gave the composition of $Pb_6Bi_2S_9$ containing a small quantity of Ag and Cu to this mineral. The phase $Pb_{5.43}Bi_{2.38}S_9$ synthesized in the present study was corresponding to natural heyrovskyite and to also synthetic Phase II described by Craig (1967)[7)], Salanci (1967)[8)], Otto and Strunz (1968)[9)], and Salanci and Moh (1969)[10)]. However, from the results of the present experiment, heyrovskyite synthesized here has not a stoichiometric composition of $Pb_6Bi_2S_9$ proposed by Klominsky et al.[6)] as mentioned above but the composition of richer in Bi_2S_3, and this phase has a narrow solid solution field along the PbS–Bi_2S_3 join from approximately 18 mol% ($Pb_{5.43}Bi_{2.38}S_9$) to 19 mol % Bi_2S_3 at 700°C.

Phase $Pb_{5.43}Bi_{2,38}S_9$ was synthesized by solid reactions between lead sulfid (PbS) and bismuth sulfide (Bi_2S_3) which were prepared from metallic lead and bismuth and

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crystalline sulfur by the same way described previousely[1]. Lead sulfide and bismuth sulfide were acculately weighed in molecular ratio of 41 to 9 and mixed thoroughly in an agate mortar under acetone. The mixture was sealed in the silica glass tube, 8 mm in inside diameter, under vacuum of 10^{-3} mmHg. The sealed glass tube was heated in an electric furnace at 750°C for 7 days. Generally almost homogeneous lead-bismuth sulfosalt mineral was obtained by the first heating. After the heating, a product was taken out from the silica glass tube and mixed under acetone in an agate mortar to prevent oxidation. Then it was again sealed in the evacuated silica glass tube and reheated at 750°C for 8 days. The charge was quenched in cold water after the second heating. The synthesized products were fully sintered aggregate of acicular crystals and megascopically lead gray in color with metallic luster.

Under the ore microscope, synthetic heyrovskyite has a weak pleochroism changing its color from white to light grayish white in air, and shows a strong anisotropism with its interference color from dark bluish gray to yellowish gray under crossed nicols. When etched by HNO_3 (1: 1), it quickly stains to black. By HCl (1: 1), it is weakly tarnished to brown. But it is negative for KOH (sat.), $HgCl_2$ (20%), $FeCl_3$ (20%), and KCN (20%). These results are in good agreement with those of natural heyrovskyite by Klominsky et al. (1971)[6].

X-ray powder diffraction data for synthetic heyrovskyite are given in Table 1,

Table 1. The X-ray powder diffraction data for the synthetic $Pb_{5.43}Bi_{2.38}S_9$ (heyrovskyite)

(1)				(2)		(3)	
I	d (meas.)	hkl	d (calc.)	I	d	I	d
1	7.80	040	7.84	2	7.94	—	—
3	4.62	250	4.620	5	4.64	—	—
5	3.93	111	3.931	10	3.934	—	—
2	3.84	121	3.841	3	3.844	—	—
20	3.74	270	3.745	20	3.751	4	3.75
6	3.70	131	3.705	5	3.705	—	—
25	3.53	141	3.536	30	3.537	3	3.53
100	3.40	400 280 410	3.417 3.399 3.397	100	3.409	10	3.41
50	3.349	151 420	3.349 3.339	30	3.348	4	3.35
2	3.258	430	3.248	3	3.255	—	—
6	3.157	161	3.157	5	3.157	—	—
1	3.134	0 10 0 440	3.134 3.132	1	3.138	—	—
35	3.103	290	3.103	15	3.106	2	3.11
6	3.066	301	3.064	5	3.064	0.5	3.07
23	3.009	321	3.007	15	3.007	3	3.01
65	2.942	331	2.940	30	2.942	4	2.94
50	2.854	341	2.854	30	2.854	4	2.85
55	2.850	2 10 0	2.849				
1	2.744	351	2.753	2	2.754	—	—

7	2.646	361	2.643	5	2.644	0.5	2.64
4	2.635	2 11 0	2.630	2	2.633	—	—
2	2.612	0 12 0	2.612	3	2.614	—	—
1	2.460	1 10 1	2.458	1	2.457	—	—
2	2.443	2 12 0	2.440	1	2.440	—	—
2	2.415	381	2.414	2	2.414	—	—
5	2.315	1 11 1	2.313	7	2.314	—	—
2	2.272	511	2.275	1	2.277	—	—
3	2.240	0 14 0	2.239	2	2.239	—	—
1	2.233	531	2.229	2	2.230	—	—
35	2.180	1 12 1	2.181	20	2.181	3	2.18
12	2.144	551	2.144	10	2.145	0.5	2.15
75	2.091	561 660	2.091 2.088	40	2.092	4	2.09
15	2.068	002	2.070	20	2.069	3	2.07
15	2.060	1 13 1	2.060	10	2.060	—	—
30	2.032	571 670	2.033 2.031	20	2.034	2	2.04
20	1.958	0 16 0	1.959	10	1.9608	1	1.96
1	1.909	591 690	1.908 1.907	5	1.9095		
7	1.894	3 13 1	1.895	15	1.8960	1	1.89
1	1.872	4 14 0	1.873	2	1.8739	—	—
5	1.844	5 10 1	1.844	10	1.8461	1	1.85
11	1.808	272 3 14 1	1.812 1.808	25	1.8097	—	—
16	1.782	4 15 0 5 11 1	1.783 1.781	30	1.7833	2	1.78
33	1.766	701 412 282	1.766 1.768 1.768	40	1.7672	2	1.77
5	1.754	422 721	1.759 1.755	10	1.7577	—	—

(1) Synthetic $Pb_{5.43}Bi_{2.38}S_9$ (heyrovskyite), values of d-calc. were calculated by the cell constant as follows; a=13.70, b=31.35, c=4.14 A.

(2) Synthetic $Pb_{5.49}Bi_{2.34}S_9$ by Otto and Strunz (1968).

(3) Synthetic $Pb_{5.43}Bi_{2.38}S_9$ by Craig (1967).

compared with synthetic Phase II by Otto and Strunz (1968)[9], and Craig (1967)[7]. Cell constant was calculated from the index data by Otto and Strunz (1968)[9] and was a=13.68Å, b=31.34 Å, c=4.14 Å, V=1774.95 Å^3. The density of the synthetic heyrovskyite, measured by the Berman density balance in carbon tetrachloride, was 7.12 g/cm^3 and calculated density from the cell constant was 7.15 g/cm^3 as Z=4. Both values were in good agreement with each other.

The differential thermal analysis curve of the synthetic heyrovskyite under vacuum is shown in Fig. 1. A strong endothermic peak beginning at 826°C shows a incongruent melting reaction of heyrovskyite to lillianite and liquid. This melting temperature is in good agreement with 825°±5°C which determined by Salanci and Moh (1969)[10].

Stability field of synthetic heyrovskyite at low temperature was determined by the quenching experiment. The synthetic heyrovskyite changes its composition to metal

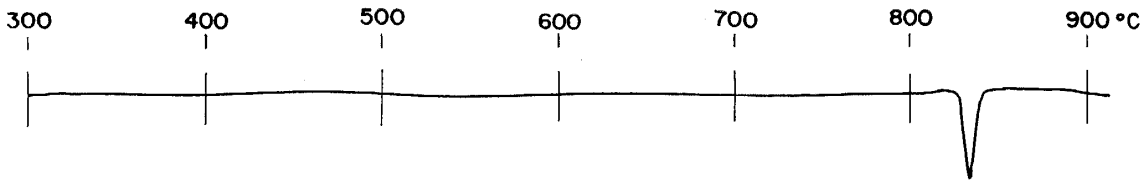

Fig. 1 The differential thermal curve for synthetic $Pb_{5.43}Bi_{2.38}S_9$ (heyrovskyite)

rich below the temperature at 485°±5°C, therefore it looks to be decomposed into galena and lillianite on the PbS–Bi_2S_3 join. The shift of the composition of this phase from the PbS–Bi_2S_3 join were also recognized by Salanci and Moh (1969) and they gave 475°±25°C for this temperature which was in good accordance with ours.

3. $Pb_{2.92}Bi_{2.05}S_6$ (Lillianite)

Existence of lillianite as mineral had been discussed long time, but after the redefinition by Ontoev (1958)[12] lillianite has been regarded as varid mineral species, and then many occurrences have been reported Syritso and Senderova (1964), Malakhov et al. (1968)[13], Kato and Sakurai (1974)[14], etc. Ideal composition of lillianite is $Pb_3Bi_2S_6$ and this mineral is corresponding to the Phase III synthesized by Craig (1967)[7], Salanci (1967)[8], Otto and Strunz (1968)[9], and Salanci and Moh (1969)[10].

Phase $Pb_{2.92}Bi_{2.05}S_6$ was synthesized by reactions between lead sulfide and bismuth sulfide in solid state. These two sulfides were acculately weighed with molecular ratio of 74 to 26, mixed thoroughly under acetone, and sealed in the evacuated silica glass tube. The tube was kept in the electric furnace at 600°C for 6 days. The product was taken out and ground under acetone in the agate mortar after heating. It was again sealed in the evacuated silica glass tube and heated at 600°C for 11 days. After second heating, it was quenched in cold water. The synthesized product was a sintered

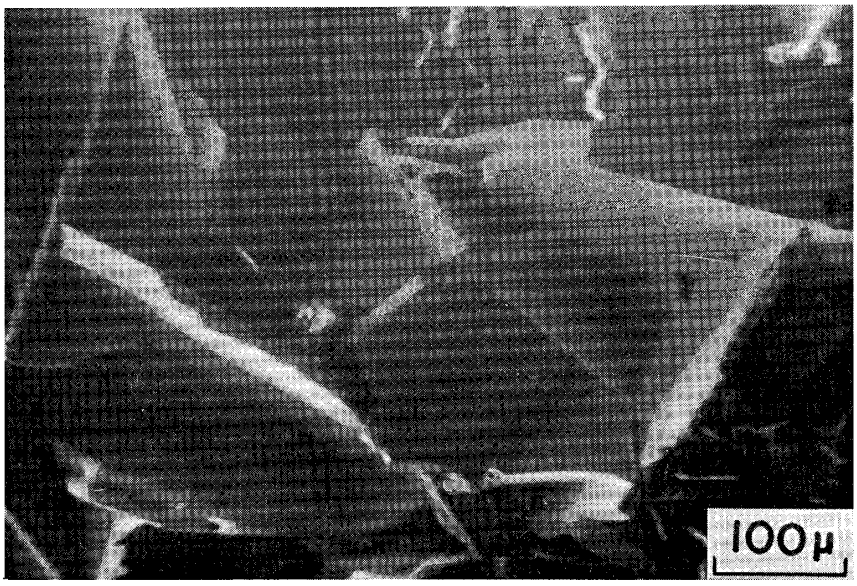

Fig. 2 Scanning electron micrograph of tablar crystals of synthetic lillianite.

Table 2. The data of X-ray powder diffraction for synthetic $Pb_{2.92}Bi_{2.05}S_6$ (lillianite)

(1)				(2)		(3)	
I	d(mes.)	hkl	(calc.)	I	d	I	d
3	10.3	020	10.31	—	—	—	—
2	5.16	040	5.15	—	—	—	—
13	4.10	240	4.099	35	4.10	2	4.10
4	3.94	101	3.941	20	3.934	0.5	3.92
3	3.87	111	3.871	10	3.880	—	—
27	3.68	121	3.681	40	3.678	2	3.67
100	3.52	250	3.520	100	3.523	10	3.52
60	3.419	131	3.419	70	3.419	4	3.42
30	3.387	400	3.382	30	3.384	3	3.39
17	3.342	410	3.338	30	3.326	2	3.35
4	3.218	420	3.214	10	3.211	0.5	3.23
—	—	—	—	—	—	0.5	3.21
13	3.132	141	3.130	30	3.128	1	3.12
15	3.065	260	3.063	30	3.060	2	3.06
50	3.010	311	3.009	60	3.005	3	3.00
75	2.918	321	2.917	80	2.913	3.5	2.91
—	—	—	—	—	—	1	2.85
40	2.783	331	2.781	60	2.778	2	2.77
13	2.703	270	2.700	40	2.669	—	2.70
4	2.579	080	2.576	5	2.575	0.5	2.58
4	2.448	351	2.448	10	2.447	—	—
15	2.359	171	2.359	40	2.357	1	2.36
2	2.248	511	2.248	—	—	—	—
2	2.223	470	2.221	5	2.220	—	—
45	2.156	181	2.156	50	2.156	3	2.15
35	2.150	531	2.148	30	2.147		
40	2.070	541	2.071	60	2.070	—	—
45	2.066	640	2.066	30	2.065	3.5	2.06
50	2.060	0 10 0 002	2.061 2.060	50	2.058	—	—
21	1.980	551 191 650	1.983 1.980 1.978	50	1.9815 1.9786	1	1.98
16	1.966	381	1.966	30	1.9645	1	1.96
7	1.896	490	1.896	20	1.8978	1	1.89
7	1.890	561	1.889	20	1.8867	—	—
7	1.885	660	1.885				
5	1.839	242	1.841	5	1.8374	—	—
9	1.830	391	1.830	20	1.8281	1	1.83
8	1.793	571	1.794	20	1.7911	—	—
35	1.777	252	1.778	7	1.7765	—	—
17	1.759	4 10 0	1.760	3	1.7590	—	—
13	1.751	412 701	1.753 1.750	2	1.7499	—	—
9	1.744	711	1.744	1	1.7421	—	—
5	1.725	721	1.725	1	1.7230	—	—
6	1.708	262	1.709	2	1.7089	—	—

(1) Synthetic $Pb_{2.92}Bi_{2.05}S_6$ (lillianite), indicies were calculated by the cell constant as follows; orthorhombic, a=13.53, b=20.61, c=4.12 Å.

(2) Synthetic $Pb_{2.82}Bi_{2.14}S_6$ by Otto and Strunz (1968).

(3) Synthetic $Pb_{2.84}Bi_{2.10}S_6$ by Craig (1967).

aggregate of acicular or tabular crystals and megascopically lead gray in color with metallic luster. Secondary electron micrograph of tabular cyrstals of synthesized lillianite are shown in Fig. 2.

Under the ore microscope, synthetic lillianite has a similar optical properties to those of other synthetic lead-bismuth sulfosalts, and shows a weak pleochroism changing its color from white to white with bluish tint in air, and a strong anisotropism with its interference color from dark gray with bluish tint to yellowish gray under crossed nicols. When etched by HCl (1: 1), it is slowly stained to brown. By HNO_3 (1: 1), KOH (sat.), $HgCl_2$ (20%), $FeCl_3$ (20%), KCN (20%), it is negative.

The X-ray powder diffraction data for synthetic lillianite are given in Table 2, comparing with synthetic Phase III by Otto and Strunz (1969) and Craig (1968). From single crystal data for synthetic lillianite measured on oscillation and Weissenberg photographs, this phase has the following cell constant; orthorhombic, $a=13.53$ Å, $b=20.61$ Å, $c=4.12$ Å, $V=1148.88$ Å^3, space group Bbmm. These values are in good agreement with the previous data. The d-values calculated from the cell parameters mentioned above are also shown in Table 2 for a comparison to the measured one. The density of synthetic lillianite was measured by the Berman density balance and was 7.07 g/cm^3, while the calculated density from the cell constant as $Z=4$ was 7.05 g/cm^3.

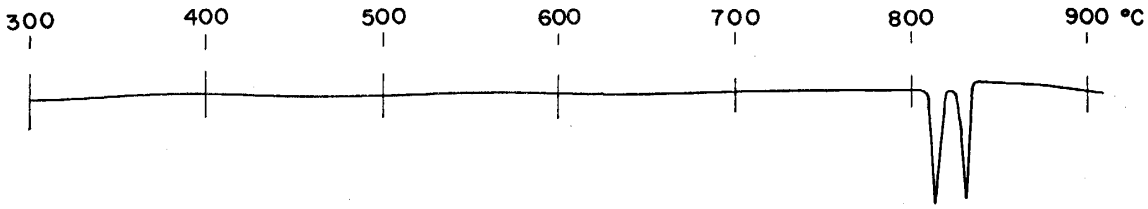

Fig. 3 The differential thermal curve for synthetic $Pb_{2.92}Bi_{2.05}S_6$ (lillianite).

The differential thermal analysis curve for synthetic lillianite in vacuum are shown in Fig. 3. Two endothermic peaks were observed. The first endothermic peak beginning at 810°C indicates a incongruent melting reaction of lillianite to heyrovskyite and liquid, and the second one beginning at 827°C shows a incongruent melting reaction of heyrovskyite to galena and liquid. From the phase study of the PbS–Bi_2S_3 system, this phase has a solid solution field extending from 25 to 28 mol% Bi_2S_3 at 600°C and from 27 to 31 mol% Bi_2S_3 at 750°C along the binary join.

4. $PbBi_2S_4$ (Galenobismutite)

Galenobismutite has been well known as a lead bismuth sulfosalt mineral, and also synthesized artificially by Craig (1967)[7], Salanci and Moh (1969)[10] and others.

Lead sulfide and bismuth sulfide were exactly weighed in the molecular ratio of one to one and mixed throughly under acetone in the agate mortar. The mixture sealed in the evacuated silica glass tube and was heated in the electric furnace kept at 600°C for 7 days. After heating, the content was taken out and ground into powder in the

agate mortar under acetone and mixed completely. Then it was again sealed in the evacuated silica glass tube and heated at 600°C for 14 days. After the second heating, it was instantly quenched in cold water. The synthesized product is a sintered aggregat of acicular crystals and megascopically lead gray in color with metallic luster.

Under the ore microscope, it is slightly lighter than bismuthinite in color and has a pleochroism changing its color from white to grayish white with yellowish tint in air, and shows strong anisotropic property with its interference color from yellowish brown to dark brownish gray under crossed nicols. When etched by $HgCl_2$ (20%), it is slowly tarnished to brown, and by HNO_3 (1 : 1), HCl (1 : 1), KOH (sat.), $FeCl_3$ (20%), and KCN (20%), it is negative. These optical properties are generally in agree with those of natural galenobismutite described by Uytenbogaardt and Bruke (1971)[15] and Schouten (1962)[17], but etching reactions are a little different from those by Uytenbogaardt (1951)[16].

The X-ray powder diffraction data for synthetic galenobismutite are shown in Table 3, comparing with synthetic and natural galenobismutites. The cell constant measured on oscillation and Weissenberg photographs for a acicular single crystal of the phase was following dimensions; orthorhombic, a=11.81 Å, b=14.57 Å, c=4.075 Å, V=701.19 Å^3, and space group Pnam. The d-values calculated from the cell parameter are given in Table 3 for the comparison with measured ones. The density measured by the Berman density balance was 7.14 g/cm^3 and the calculated density was 7.15 g/cm^3

Table 3. The X-ray powder diffraction data for synthetic $PbBi_2S_4$ (galenobismutite)

(1)				(2)		(3)	
I	d(meas.)	hkl	d(calc.)	I	d	I	d
3	7.33	020	7.303	—	—	—	—
11	4.58	220	4.595	13	4.59	1	4.55
4	4.47	130	3.502	—	—	—	—
11	3.92	011	3.921	—	—	0.5	3.93
—	—	—	—	20	3.80	—	—
3	3.83	111	3.721	—	—	—	—
45	3.64	040	3.651	30	3.65	3	3.65
100	3.46	140 320	3.489 3.468	100	2.47	10	3.45
50	3.402	121	3.405	57	3.41	—	—
38	3.351	201	3.352	40	3.36	0.5	3.36
16	3.267	211	3.261	10	3.27	0.5	3.27
7	3.052	330 221	3.063 3.046	—	—	—	—
39	3.015	131	3.019	40	3.02	4	3.03
2	2.964	400	2.956	—	—	—	—
4	2.892	410	2.897	—	—	—	—
2	2.828	150	2.836	—	—	—	—
12	2.776	311	2.779	17	2.78	3	2.76
21	2.758	231	2.761	20	2.76	—	—
14	2.734	420	2.740	13	2.74	—	—
4	2.673	340	2.678	—	—	—	—

18	2.644	{141 321	{2.649 2.640	13	2.65	—	—
2	2.611	250	2.619	—	—	—	—
5	2.520	430	2.527	—	—	—	—
37	2.467	241	2.469	33	2.47	4	2.46
10	2.446	331	2.447	16	2.45	—	—
25	2.390	401	2.392	16	2.39	2	2.39
4	2.332	350	2.347	—	—	—	—
4	2.325	510	2.334	—	—	—	—
4	2.299	421	2.273	—	—	—	—
16	2.247	260	2.251	13	2.25	1	2.24
18	2.200	251	2.202	10	2.20	1	2.20
3	2.145	431	2.147	—	—	—	—
16	2.067	360	2.071	13	2.07	4	2.05
16	2.055	161	2.057	13	2.05	—	—
9	2.051	170	2.055	13	2.04	—	—
20	2.038	002	2.035	—	—	—	—
12	2.037	351	2.033	—	—	—	—
17	2.023	511	2.025	17	2.02	0.5	2.01
9	2.018	012	2.015	—	—	—	—
13	2.000	441	2.000	13	1.999	—	—
6	1.995	112	1.987	—	—	—	—
3	1.982	540	1.985	—	—	—	—
52	1.968	{261 521 600	{1.970 1.969 1.971	57	1.966	5	1.961
1	1.950	610	1.953	—	—	—	—
12	1.885	531	1.885	13	1.881	2	1.881
9	1.877	460	1.879	—	—	—	—
4	1.872	—	—	—	—	—	—
1	1.863	222	1.861	—	—	—	—
7	1.850	451	1.850	—	—	0.5	1.848
7	1.844	370	1.844	—	—	—	—
5	1.832	550	1.838	—	—	—	—
8	1.825	080	1.826	—	—	—	—
10	1.802	180	1.804	13	1.880	—	—
12	1.797	541	1.784	10	1.779	0.5	1.784
7	1.778	271	1.771	—	—	—	—
32	1.759	322	1.755	30	1.757	3	1.762
16	1.754	280	1.744	—	—	—	—
12	1.731	640	1.734	17	1.731	1	1.734
8	1.704	{461 470	{1.706 1.705	—	—	—	—
5	1.699	—	—	—	—	—	—
2	1.665	631	1.666	—	—	—	—
5	1.647	181	1.649	—	—	—	—
3	1.643	720	1.645	—	—	—	—
3	1.640	650	1.634	—	—	—	—
3	1.571	471	1.572	—	—	—	—

(1) Synthetic $PbBi_2S_4$ (galenobismutite), cell constant is follows: orthorhombic, a=11.82, b=14.60, c=4.06 Å.

(2) Synthetic $Pb_{0.89}Bi_{1.04}S_4$ by Salanci and Moh (1969).

(3) Natural galenobismutite from Cariboo Gold Quartz mine, B. C. by Berry and Thompson (1962).

as $Z=4$. These data are in good agreement with those of natural galenobismutite described by Berry and Thompson (1962)[18].

The differential thermal analysis was examined on the synthetic galenobismutite in the evacuated silica glass tube. The DTA curve shown in Fig. 4 has two endothermic peaks. The first peak beginning at 752°C is corresponding to the incongruent melting reaction of galenobismutite to lillianite and liquid, and the second one with the end point at 800°C indicates a liquidus temperature.

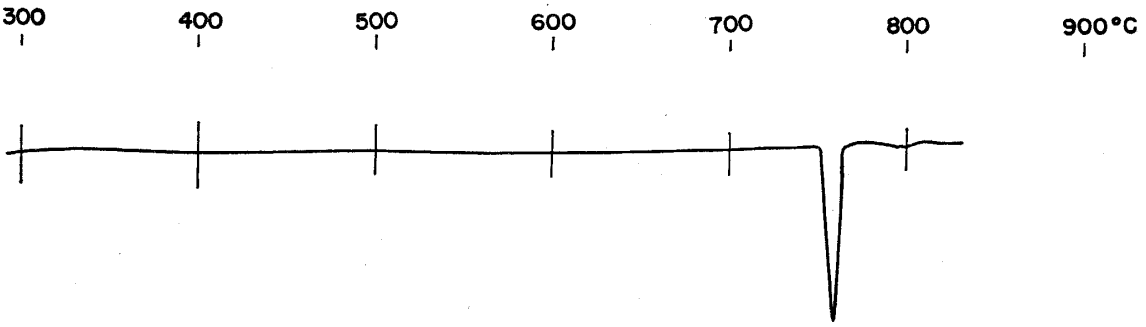

Fig. 4 The curve of the differential thermal analysis for synthetic $PbBi_2S_4$ (galenobismutite).

From the phase study of the PbS–Bi_2S_3 system galenobismutite looks unstable on this binary join because $Pb_2Bi_2S_5$ and bismuthinite assemblage exists stably below approximately 465°C. However galenobismuthite shifts its composition around this temperature towards rich in sulfur and is stable practically at lower temperatures.

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