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INVESTIGATIONS ON THE TERNARY SYSTEM Ag-P-S AND THERMAL BEHAVIOUR OF THE COMPOUNDS

H. Andrae and R. Blachnik

ANORGANISCHE CHEMIE, UNIVERSITÄT OSNABRÜCK, BARBARASTR. 7, D-4500 OSNABRÜCK

Parts of the ternary system Ag-P-S were investigated by DTA- and X-ray measurements. The quasibinary section of Ag_2S-P_4S_{10} is described. The thermal behaviour and X-ray diffraction patterns of Ag_7PS_6, Ag_3PS_4, $Ag_7P_3S_{11}$, $Ag_4P_2S_7$ and $Ag_2P_2S_6$ were studied. DTA-diagrams and X-ray powder data are given.

Introduction

Metal thiophosphates can be prepared by reaction of metal sulphides or metal chlorides with P_4S_{10} [1, 2] or by synthesis from the elements at high temperatures [3-12].

It depends on composition, reaction conditions and the prefered valence state of the metal [13, 14], which kind of metal thiophosphate (IV) or (V) will be formed.

The primary interest in recent investigations was to prepare new compounds, to examine their crystal structure and vibrational spectroscopic data. There are few publications [2, 5, 10] which deal with phase relations in ternary systems or the thermal behaviour of the metal thiophosphates.

This paper presents some results of DTA- and X-ray- investigations in the ternary system Ag-P-S. The phase relations of the quasibinary section Ag_2S-P_4S_{10} will be described.

Experimental

High-purity elements (Ag: 99.999%, Degussa; P: ultrapure, electronic grade, Hoechst AG, Werk Knappsack; S: chem. pure,

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cryst., Riedel-De-Haën AG) were mixed in stoichiometric amounts(≈ 1 g total) for the preparation of the compounds. After sealing in evacuated quartz ampoules, the reactants were heated first to the melting point of the mixtures and shaken vigorously to homogenize the melt. The samples were then annealed at 403, 513, 623 and 773 K for periods between two weeks and two month and quenched afterwards to ambient temperature.

Results

The quasibinary section Ag_2S-P_4S_{10}

The phase diagram of the system, shown in fig. 1, contains several eutectic and peritectic reactions.

Ag_7PS_6 melts congruently. The silver thiophosphates Ag_3PS_4, $Ag_7P_3S_{11}$, $Ag_4P_2S_7$ and $Ag_2P_2S_6$ decompose by peritectic reactions, the eutectic compositions and temperatures were determined to 3.5 mole-% P_4S_{10} and 1011 K for the Ag_2S-Ag_7PS_6 eutectic and 96 mole-% P_4S_{10} and 542 K for the $Ag_2P_2S_6$-P_4S_{10} eutectic. Solid solutions, based on Ag_2S and P_4S_{10}, were not observed. Above the monotectic temperature of 713 K a liquid miscibility gap appears in the system with the monotectic point at 63 mole-% P_4S_{10}. The binodal curve (dotted line) was assumed, since no experimental determinations were made.

The compounds of particular interest are Ag_7PS_6, Ag_3PS_4, $Ag_7P_3S_{11}$, $Ag_4P_2S_7$ and $Ag_2P_2S_6$. A series of DTA- and DSC-measurements have been performed to establish their thermal behaviour. The relevant data are compared with literature values in table 1.

X-ray powder data were measured by means of room- and high-temperature X-ray-Guinier technique and powder diffractometer methods. A listing of lattice constants is given in table 2 for each compound.

Table 1 Thermal data of the silver thiophosphates in the quasibinary section Ag_2S–P_4S_{10}

Compound	T_1 [K]	T_2 [K]	T_3 [K]	T_4 [K]	Reference
Ag_7PS_6		539 ± 2 538 ± 2		1092 ± 5 1065 ± 5	[5]
Ag_3PS_4		783	803 ± 2	930 ± 5	[2]
$Ag_7P_3S_{11}$	574 ± 2		857 ± 2		
$Ag_4P_2S_7$		700 ± 2	740 ± 2		
$Ag_2P_2S_6$			719 ± 2		

T_1 ≙ eutectoid temperature
T_2 ≙ crystal transition temperature
T_3 ≙ decomposition temperature
T_4 ≙ melting temperature

Table 2 Crystal structure data of the silver thiophosphates in the quasibinary section Ag_2S–P_4S_{10}

Compound	Ag_7PS_6	Ag_7PS_6	Ag_3PS_4	$Ag_7P_3S_{11}$	$Ag_4P_2S_7$	$Ag_4P_2S_7$	$Ag_2P_2S_6$
Modification	LTM	HTM			LTM	HTM	
Crystal system	cubic	cubic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_13$	$F\bar{4}3m$	$Pmn2_1$	B 2/b	B 2/b		B 2/m
Lattice constants [pm; °]	a=1039.45(9)		a=765.0(1) b=686.8(1) c=650.9(1)	a=2398.1(8) b=2489.8(8) c= 635.4(3) γ= 110.91(4)	a=1078.8(4) b=1621.1(4) c= 653.8(1) γ= 106.80(2)	a= 807.3(2) b=1102.2(3) c= 636.8(2) β=105.22(3)	a=1123.8(1) b= 674.2(2) c= 701.8(2) γ= 126.96(2)
Lattice constants reference data [pm; °]	a=1036 [3] a=1039.7(2) [5] a=1040.2 [17]	a=1048.6(5) [5]		a=2397.1(1) b=2488.1(1) c= 636.1(4) γ= 110.85(5) [7, 16]	a=1077.8(5) b=1621.1(8) c= 653.4(3) γ= 106.8(1) [8]		a=1121.0(3) b= 673.1(2) c= 699.8(2) γ= 126.84(2) [12]

Note. Standard deviations are given in parentheses.

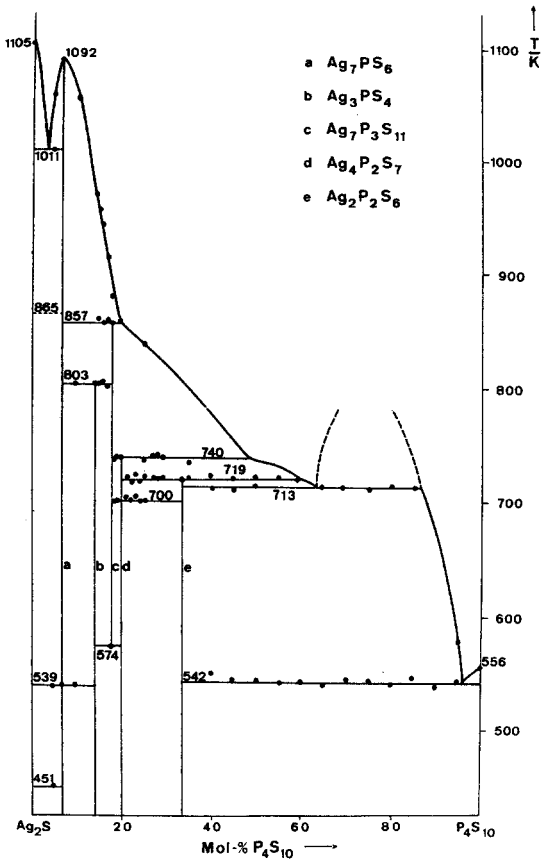

Fig. 1 The quasibinary section Ag_2S-P_4S_{10}

The silver thiophosphate Ag_7PS_6

The black compound was synthesized from the elements at 1123 K. It belongs to the argyrodite family of tetrahedrally close-packed structures and occurs in two modifications. The reversible phase transition takes place at 539 K. The high-temperature form is not quenchable. The compound melts at 1092 K without decomposition. The DTA-diagram of Ag_7PS_6 is shown in fig. 2.

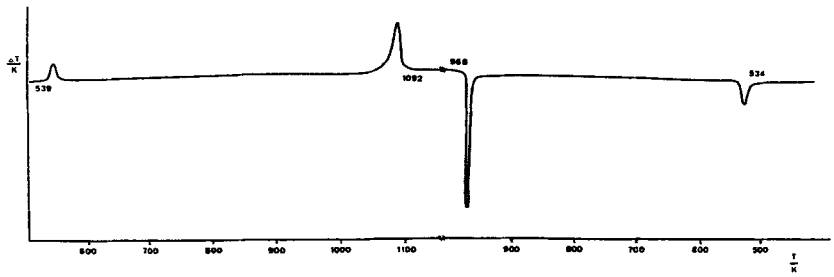

Fig. 2 DTA-diagram of Ag_7PS_6

The low-temperature modification of Ag_7PS_6 belongs to the cubic space group $P2_13$. The high-temperature form crystallizes like the isotypic Ag_7PSe_6, Ag_7SbS_6 [4, 5], Ag_7AsS_6 and Ag_7AsSe_6 [15] in the space group $F\bar{4}3m$.

Recent high-temperature Guinier photographs[5] indicate that the phase transition is of the order-disorder type, a superstructure is formed at low temperatures. The calculated lattice constants and literature data are given in table 2.

The silver orthothiophosphate Ag_3PS_4

Ag_3PS_4 was synthesized by the following methods; high-temperature reaction of the elements or conversion of $Ag_2P_2S_6$ by adding proper amounts of silver and sulfur and heating. DTA-examination of the compound (see fig. 3) revealed three thermal effects at 803, 857, and 972 K. The first one is caused by the peritectoid decomposition of Ag_3PS_4 to Ag_7PS_6 and $Ag_7P_3S_{11}$, the second peak by the peritectic reaction of $Ag_7P_3S_{11}$ to Ag_7PS_6 and melt. The third effect corresponds to the intersection of the liquidus line.

Powder diffraction measurements were used to refine the unit cell dimensions and to verify the structure type. Fig. 4 shows the powder diffraction diagram, corresponding lattice parameters and intensities are summarized in table 3.

Brockner et al. [2] suggest by the similarity of the Ag_3PS_4 Raman spectrum to Cu_3PS_4 a structure based on the enargite-type. The X-ray diffraction data of Ag_3PS_4 were simulated using the orthorhombic space group $Pmn2_1$ of the

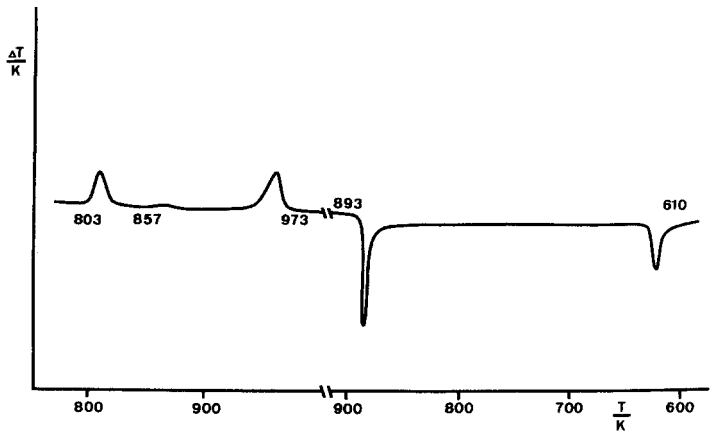

Fig. 3 DTA-diagram of Ag_3PS_4

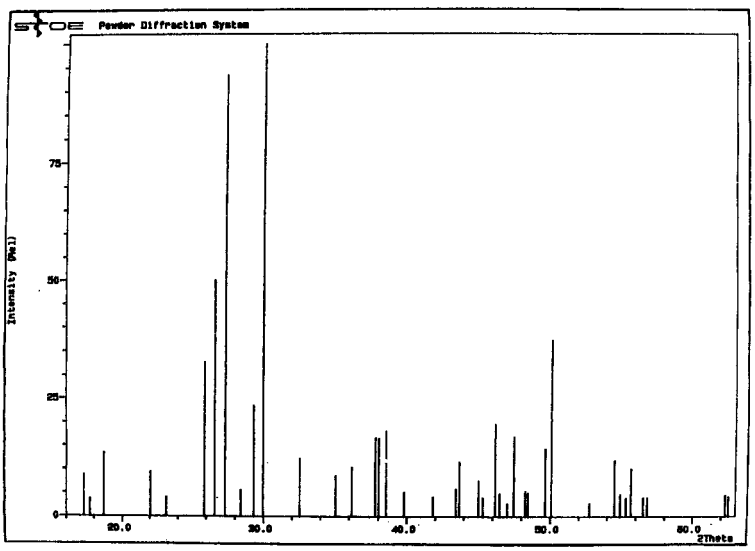

Fig. 4 Powder diffraction diagram of Ag_3PS_4

enargite Cu_3AsS_4 [18-20] and also compared with the X-ray parameters of Cu_3PS_4 [21] Both methods show acceptable agreement with the experimental powder diffraction data, so that the assumption of Brockner [2] could be confirmed.

Table 3 Powder diffraction pattern of Ag_3PS_4

d_{obs} [pm]	d_{calc} [pm]	h k l	I	d_{obs} [pm]	d_{calc} [pm]	h k l	I
510.91	511.06	1 1 0	8.9	207.91	207.84	1 3 1	5.9
495.78	495.71	1 0 1	3.8	206.91	206.87	0 1 3	11.6
472.09	472.42	0 1 1	13.4	201.10	200.98	2 2 2	7.6
401.65	401.95	1 1 1	9.5	196.34	196.44	2 3 0	19.5
343.24	343.41	0 2 0	32.7	191.22	191.25	4 0 0	16.8
334.35	334.17	2 1 0	50.1	187.21	187.24	0 3 2	5.0
325.35	325.42	0 0 2	93.4	183.34	183.41	0 2 3	14.3
313.59	313.29	1 2 0	5.6	181.90	181.97	2 1 3	37.3
303.74	303.72	0 2 1	23.5		181.85	1 2 3	
297.34	297.28	2 1 1	100.0	173.26	173.29	3 2 2	2.9
282.41	282.29	1 2 1	3.2	168.15	168.17	2 3 2	11.9
274.62	274.50	1 1 2	12.2	167.00	167.08	4 2 0	4.7
255.65	255.53	2 2 0	8.6	166.06	166.02	0 4 1	4.0
247.96	247.86	2 0 2	10.4	165.43	165.38	2 2 3	10.1
237.43	237.43	3 0 1	16.7	162.67	162.71	0 0 4	4.1
236.16	236.21	0 2 2	16.5	161.91	161.84	4 2 1	4.1
233.19	233.14	2 1 2	18.1	148.59	148.64	4 2 2	4.3
225.72	225.70	1 2 2	5.2	134.36	134.40	0 5 1	3.1

The silver thiophosphate $Ag_7P_3S_{11}$

In 1982 Toffoli et al. [7, 16] report the synthesis and the crystal structure of $Ag_7P_3S_{11}$. A special feature of the structure is the coexistence of PS_4^{3-}- and $P_2S_7^{4-}$- groups.

$Ag_7P_3S_{11}$ crystallizes in the space group B2/b. The published lattice parameters are compared with our data in table 2.

Room-temperature Guinier photographs of a mixture with the composition of $Ag_7P_3S_{11}$, annealed at 513 K, show X-ray reflections of Ag_3PS_4 and the high-temperature form of $Ag_4P_2S_7$. DSC-investigations verify that $Ag_7P_3S_{11}$ is a high-temperature compound with an eutectoid temperature of 574 K. Difference

thermal analysis (see fig. 5) yields a second thermal effect at 857 K, which corresponds to the peritectic decomposition of the compound to Ag_7PS_6 and melt.

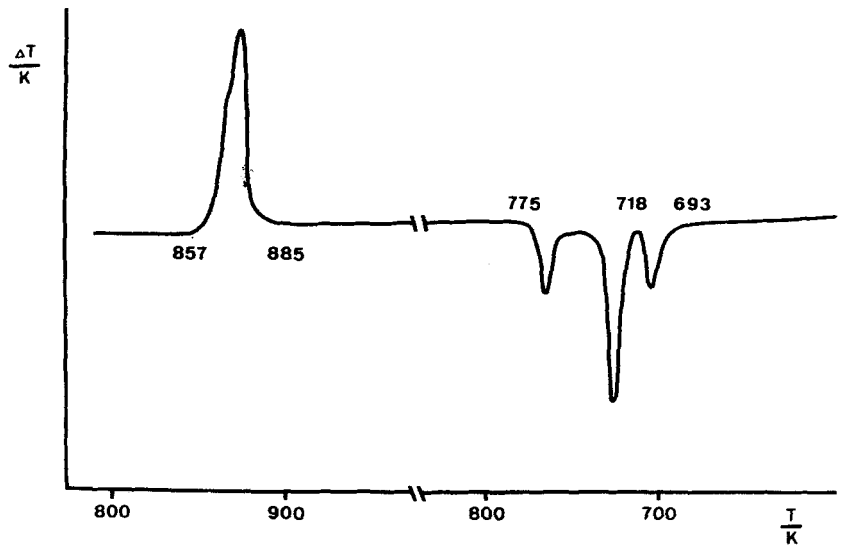

Fig. 5 DTA-diagram of $Ag_7P_3S_{11}$

The silver pyrothiophosphate $Ag_4P_2S_7$

$Ag_4P_2S_7$ was prepared by high-temperature reaction of the elements. DTA-measurements (see fig. 6) of the compound revealed two thermal effects at 700 and 740 K. The first one corresponds to the crystal transition of $Ag_4P_2S_7$, the second effect results from its peritectic reaction to $Ag_7P_3S_{11}$ and melt.

No single crystals could be obtained of both modifications. Refinement of the X-ray powder reflections of the low-temperature form gave lattice parameters similar to those of Toffoli et al.[8] (see table 2).

The calculated unit cell dimensions of the high-temperature form (α-SiO_2 was used as internal standard) are shown in table 2. The powder diffraction diagram is given in fig. 7, the d-values are summarized in table 4.

The transition from the high-temperature to the low-temperature modification is a slow process. Experimental studies show that it is therefore possible to obtain the metastable high-temperature form by slowly cooling to ambient temperature.

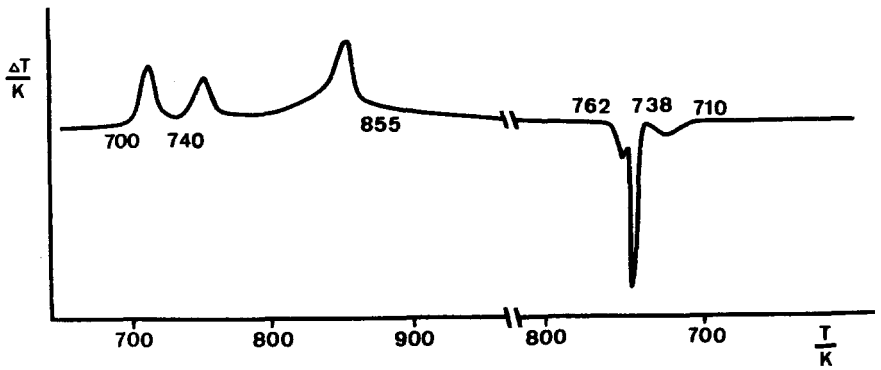

Fig. 6 DTA-diagram of $Ag_4P_2S_7$

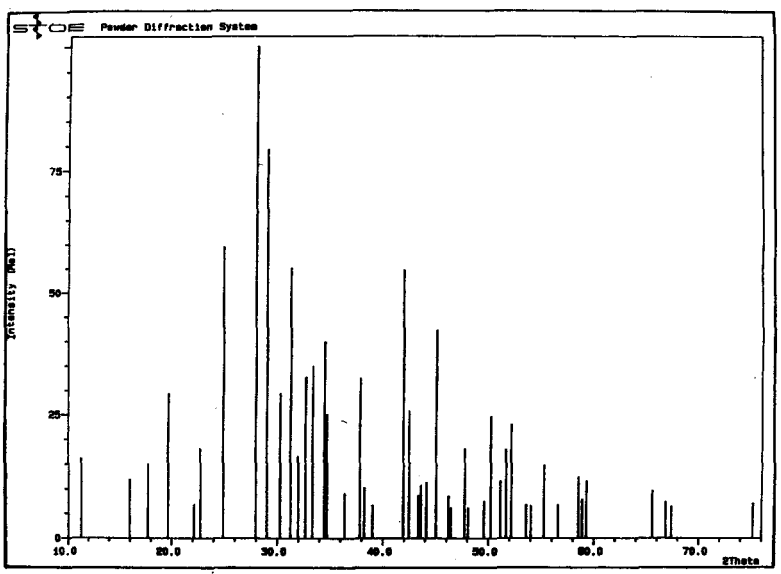

Fig. 6 Powder diffraction diagram of the high-temperature modification of $Ag_4P_2S_7$

Table 4 X-ray powder data of the high-temperature modification of $Ag_4P_2S_7$

d_{obs} [pm]	d_{calc} [pm]	h k l	I	d_{obs} [pm]	d_{calc} [pm]	h k l	I
777.57	778.95	1 0 0	16.1	237.52	237.48	1 2 2	32.4
550.78	551.09	0 2 0	11.9	230.47	230.36	2 3 1	6.7
498.11	498.57	$\bar{1}$ 1 1	15.0		230.357	$\bar{3}$ 0 2	
449.98	449.88	1 2 0	29.3	215.33	215.28	2 0 2	54.7
389.28	389.48	2 0 0	18.1	207.41	207.49	0 5 1	10.7
356.68	356.46	$\bar{2}$ 1 1	59.5	205.10	205.12	0 4 2	11.3
318.21	318.06	2 2 0	100.0	201.24	201.32	$\bar{2}$ 1 3	42.3
307.17	307.20	0 0 2	79.2	190.35	190.31	1 4 2	18.1
295.59	295.71	2 0 1	29.3	180.76	180.67	$\bar{1}$ 5 2	24.7
285.55	285.61	2 1 1	55.1	178.19	178.23	$\bar{4}$ 2 2	11.6
279.53	279.52	$\bar{2}$ 0 2	16.5	176.77	176.74	3 0 2	18.0
273.68	273.77	$\bar{1}$ 2 2	32.7		176.734	2 5 1	
268.34	268.33	0 2 2	34.9		176.733	$\bar{3}$ 4 2	
259.90	259.77	1 4 0	39.9	175.95	176.00	0 6 1	23.0
258.23	258.09	$\bar{3}$ 1 1	25.1				

Table 5 X-ray Guinier diffraction parameters of a high-temperature compound with illdefined composition between 21 and 33 mol-% P_4S_{10} at 731 K (Internal standard: Si).

Refined lattice parameters [pm, °]
[standard deviations are given in parentheses]

Crystal system: monoclinic Lattice constants: a = 696.1[4]
b = 1409.7[4]
c = 651.3[4]
β = 112.25[5]

d_{obs} [pm]	d_{calc} [pm]	h k l	I	d_{obs} [pm]	d_{calc} [pm]	h k l	I
602.76	602.80	0 0 1	w	292.90	292.97	$\bar{2}$ 2 0	w
587.12	585.94	$\bar{1}$ 1 0	vw	265.49	265.69	2 3 0	w
558.20	558.06	$\bar{1}$ 0 1	w	258.26	258.29	$\bar{1}$ 5 0	vw
517.91	518.89	$\bar{1}$ 1 1	w	251.67	251.65	$\bar{1}$ 5 1	vw
359.97	359.45	$\bar{1}$ 3 1	w	237.99	237.77	2 4 0	vw
352.29	352.43	0 4 0	vw	234.97	234.97	0 6 0	vw
321.84	322.11	2 0 0	w	212.30	212.29	3 1 0	w
314.03	314.02	$\bar{2}$ 1 0	w	185.66	185.85	2 1 2	vw
309.16	309.19	1 4 0	vw	184.74	184.75	0 3 3	w
298.13	297.99	$\bar{1}$ 4 1	w	169.09	169.14	0 8 1	vw

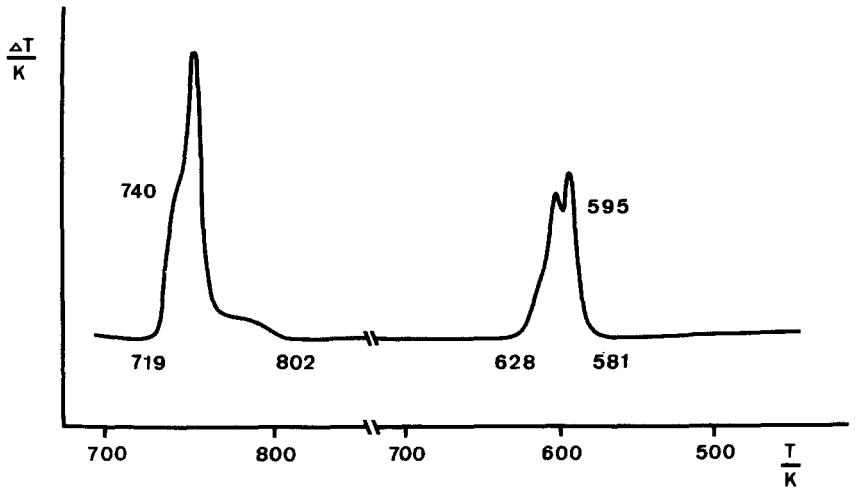

Fig. 8 DTA-diagram of $Ag_2P_2S_6$

The silver hexathiodimetaphosphate $Ag_2P_2S_6$

In recent report Thilo and Ladwig [11] suppose that the anion partial structure of the orange silver thiophosphate with the general formula $(AgPS_3)_x$ consist of straight condensed thiophosphate chains. However, a single crystal structure determination, performed by Toffoli et al. [12], shows the existence of isolated $P_2S_6^{2-}$-anion groups. $Ag_2P_2S_6$ crystallizes in a monoclinic lattice with the space group B2/m. Table 2 gives the calculated lattice parameters.

High-temperature X-ray-Guinier photographs of the compound reveal a new, unknown X-ray diffraction pattern. The lattice data of this compound with a hitherto illdefined composition at 731 K are described in table 5. We are at the moment not able to decide wether this compound is not part of the quasi-binary section or a metastable compound, because it was not found in all preparations attempts of samples with the same initial composition.

The difference thermal analysis of $Ag_2P_2S_6$ yields three thermal effects at 719, 740 and 802 K (see fig. 8). The silver hexathiodimetaphosphate decomposes at 719 K in

$Ag_4P_2S_7$ and melt. The second effect corresponds to the peritectic reaction of $Ag_4P_2S_7$ in $Ag_7P_3S_{11}$ and melt. The intersection of the liquidus line was found at 802 K. No thermal effect, due to the unknown compound, could be observed.

Acknowledgements

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Zusammenfassung - Mittels DTA- und Röntgendiffraktionsmessungen wurden Teile des Dreikomponentensystemes Ag-P-S untersucht. Es wird der quasibinäre Schnitt von Ag_2S-P_4S_{10} beschrieben. Weiterhin wurden das thermische Verhalten und die Röntgenbeugungsbilder von Ag_7PS_6, Ag_3PS_4, $Ag_7P_3S_{11}$, $Ag_4P_2S_7$ und $Ag_2P_2S_6$ untersucht. DTA-Diagramme und Röntgen-Pulverdaten werden gegeben.

Резюме - Методом ДТА и рентгеноструктурного анализа изучены отдельные части тройной системы Ag-P-S . Описана квазибинарная часть Ag_2S - P_4S_{10}. Изучено термическое поведение и рентгенограммы соединений Ag_7PS_6, Ag_3PS_4, $Ag_7P_3S_{11}$, $Ag_4P_2S_7$ $Ag_2P_2S_6$. Приведены кривые ДТА и данные порошкового рентгеноструктурного анализа.