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Dedicated to Professor Dr. H. J. Seifert on the occasion of his 60th birthday

TERNARY CHALCOGENIDE SYSTEMS X: The quasiternary system Ag_2S–Cu_2S–P_4S_{10}*

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The quasiternary system Ag_2S–Cu_2S–P_4S_{10}** was investigated by DTA- and X-ray measurements. No quasiternary compound was found. The phase diagram of the constituent binary Cu_2S – P_4S_{10} is given for the first time. It contains the compounds Cu_7PS_6, Cu_3PS_4 and $(CuPS_3)_n$. The previously reported $Cu_4P_2S_7$ was not observed. Thermal and X-ray data of these compounds are given. The compounds Cu_7PS_6 + Ag_7PS_6 and Cu_3PS_4 + Ag_3PS_4 are completely miscible in the solid state.

By the raction of phosphorous chalcogenides with an eccess of chalcogen ions, one obtains different thioanions containing tetrahedrally coordinated phosphorus. During our investigation of ternary systems of the type Ib–Vb–VIb (Ib = Cu, Ag; Vb = P, As, Sb, Bi: VIb = S, Se, Te) we looked for the thermodynamic cdonditions under which such compounds are formed. One part of this series is the quasiternary system Ag_2S–Cu_2S–P_4S_{10}** reported in this work.

Silver or copper thiophosphates can be prepared by the reaction of metal sulphides or metal chlorides with P_4S_{10} [1, 2] or by high-temperature synthesis from the constituent elements [3, 4]. The composition of the sample

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* IX: B. Legendre, B. Gather and R. Blachnik, Z. Metallk., 71 (1980) 588.

** In the following the formula Cu_2S is given instead of $Cu_{2-\delta}S$, because its small deviations from integral stoichiometry have no influence on the phase diagram.

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and the conditions of the reaction determine which type of thiophosphate is formed. The primary interest of recent publications is the preparation of new compounds and the determination of crystal structures and vibrational spectra. Little information is available on phase diagrams, although these would contain all the necessary data for preparation routes to special thiophosphates. This paper presents the first report about the qasiternary Ag_2S–Cu_2S–P_4S_{10} system, obtained by DTA and X-ray investigations.

Experimental

High-purity elements (Cu: 99.999%, Degussa: Ag: 99.999%, Degussa; Cu: 99.999%, Ventron; P: ultrapure, electronic grade, Hoechst AG, Werk Knapsack; S: chem. pure, cryst., Riedel de Haen 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 months, followed by quenching to ambient temperature. Samples (200 mg) of each product were ground to powders, evacuated in thin-walled tubes of 2–3 mm outer diameter, which were then sealed. A previously described apparatus [5] was used for the DTA measurements. The thermograms were recorded using silicon as reference material with heating and cooling rates of 10 K min^{-1}. Another part of the sample was used in the X-ray measurements (Guinier–4 (Huber), Automated Diffractometer System (Stoe) Guinier–Simon FR 533 (Enraf Nonius) CuK_α–radiation). X-ray data were evaluated by the program LSUCR [6].

Results

Data for the constituent binary systems

Ag_2S–Cu_2S was taken from Chang [7]. It is mainly based on the high temperature X-ray data of Skinner [8] and DTA measurements of Krestovnikow [9]. At higher temperatures it shows complete solid solubility. The compounds $Cu_{1+x}Ag_{1-x}S$, $Cu_{0.8}Ag_{1.2}S$ and $Cu_{0.45}Ag_{1.55}S$ crystallize from the solid solutions at temperatures below 120°.

The system Ag_2S–P_4S_{10} [10] contains five compounds. The only congruently melting compound is Ag_7PS_6 with a melting point of 1092 K, and a

phase transition at 539 K. The compounds $Ag_7P_3S_{11}$, $Ag_4P_2S_7$ and $Ag_2P_2S_6$ are peritectic with decomposition temperatures of 857(u_1), 740(u_2) and 719(u_3) K. Ag_3PS_4 decomposes in a peritectoid reaction at 803 K. The high temperature phase $Ag_3P_7S_{11}$ is formed by an eutectoid reaction at 574 K. The miscibility gap at the P_4S_{10}-rich side of the system has a monotectic temperature of 713 K. The two eutectics were found at 1011 (e_1) and at 542 K (e_2). No solid solution in the pure components was observed.

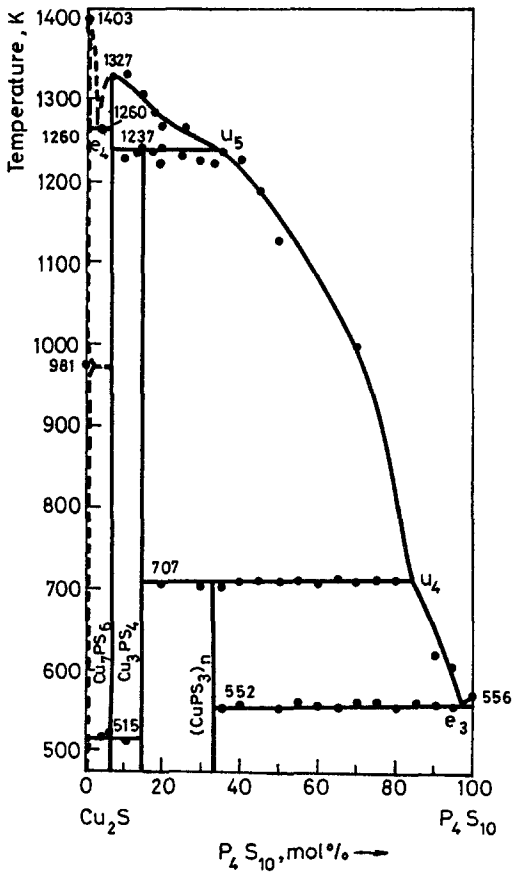

Fig. 1 The quasibinary system Cu_2S–P_4S_{10}

The phase diagram Cu_2S–P_4S_{10} has not yet been investigated. The following phase diagram (Fig. 1) was constructed using data from our thermal and X-ray measurements. Cu_7PS_6 melts congruently at 1327 K. The copper thiophosphates Cu_3PS_4 and $(CuPS_3)_n$ decompose by a peritectic reaction at

1237 K (u_5) into Cu_7PS_6 and a melt and at 707 K (u_4) into Cu_3PS_4 and a melt, respectively. The eutectic compositions and temperatures wewre determined as approximately 5 mol% P_4S_{10} and 1260 K (e_4) for the Cu_2S–Cu_7PS_6 and as 97.3 mol% P_4S_{10} and 552 K (e_3) for the $(CuPS_3)_n$ eutectic. Solid solutions based on P_4S_{10} were not observed, a very narrow homogenity range of $Cu_2{-}\delta S$ was assumed. The compounds of particular interest are Cu_7PS_6, Cu_3PS_4, $Cu_4P_2S_7$ [11, 12] and the new compound $(CuPS_3)_n$. A series of DTA and X-ray measurements have been performed to characterize these compounds, their relevant thermal and X-ray data are collected in the Tables 1 and 2. Neither by X-ray nor by thermal measurements the compound $Cu_4P_2S_7$ could be found. The X-ray powder data of $Cu_4P_2S_7$, reported by Soklakov, are strongly related to those of Cu_3PS_4. All measurements indicate the existance of $(CuPS_3)_n$, which was until now not known. We did not succeed in preparing samples of pure $(CuPS_3)_n$, therefore no indexing of its powder pattern was possible.

Table 1 Thermal data the copper thiophosphates Cu_2S–P_4S_{10}

Compound	T_1 K	T_2 K	T_3 K	Reference
Cu7PS6	515		1327	
	508		1318	[13]
Cu3PS4		1237	1302	
		1243	1278	[14]
Cu(PS3)n		707	1225	

T_1 = phase transformation temperature

T_2 = peritectic temperature

T_3 = melting or liquidus temperature

The quasiternary system Ag_2S-Cu_2S-P_4S_{10}

X-ray measurements on powdered samples were used to establish the equilibria between the various compounds of the system. The isothermal section at 673 K is given in Fig. 2. No change in the phase relations was observed in the section at 513 K, except for the disappearance of the high-temperature compound $Ag_7P_3S_{11}$. No quaternary compound was observed within our experimental conditions. Most of the ternary compounds show no homogeneity region, except for $Ag_7P_3S_{11}$, which dissolves up to 4.70 mol%

Cu_2S. Cu_7PS_6–Ag_7PS_6 and Cu_3PS_4–Ag_3PS_4 form a series of continuous solid solutions at 513 and 673 K but only the former system between the congruently melting M_7PS_6– compounds of the argyrodite type is a quasibinary cross section of the system.

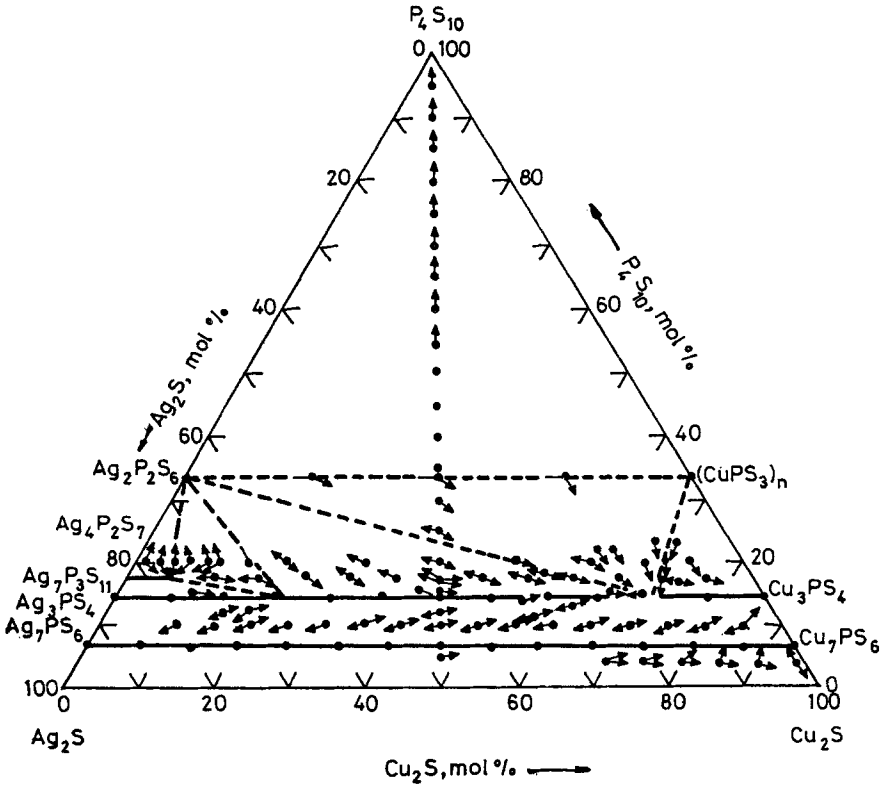

Fig. 2 Isothermal section in the system Ag_2S–Cu_2S–P_4S_{10} at 673 K (arrows point to phases which are found in the quenched samples)

The provisional liquidus projection of the space diagram (Fig. 3) gives some information about the thermal behaviour of the compounds. Starting from the peritectic points u_1–u_5 five peritectic lines stretch into the ternary surface, subdividing the dominating primary crystallization regions of the M_7PS_6 solid solution and Cu_3PS_4. These lines merge and end in the eutectic valley e_2–e_3 at the P_4S_{10} corner of the system. The primary crystallization surface of M_7PS_6 is divided from the solid solution of the type $Ag_{2-x}Cu_xS$ by the eutectic valleys e_1–s_k and s_k–e_4, which join in the critical point s_k. The reaction pathways which produce this topology are summarized in Fig. 4.

Table 2 Strucrure data of the copper thiosphates

	Cu_7PS_6		Cu_3PS_4
	low temp.	high temp.	
Space group	P213	$F\bar{4}3m$	Pmn21
Lattice constants [pm]	a = 967.09 (a)	a = 971.3 [587 K]	a = 729.67 (6) b = 632.65 (4) c = 607.22 (8) (single crystal data)
Lattice constants [pm] (reference data)	a = 966.9 (2) [15]	a = 971 (2) [508 K] [13]	a = 729.6 (2) b = 631.9 (2) c = 607.2 (2) [16] (powder data)
Linear coefficent of thermal expansion $[K^{-1}]$	a = 23.32 [500 K]	a = 28.32 [530 K]	

The quasibinary section Ag_7PS_6–Cu_7PS_6 is given in Fig. 5 and shows complete miscibility in the solid and liquid state. The liquidus curve is con-

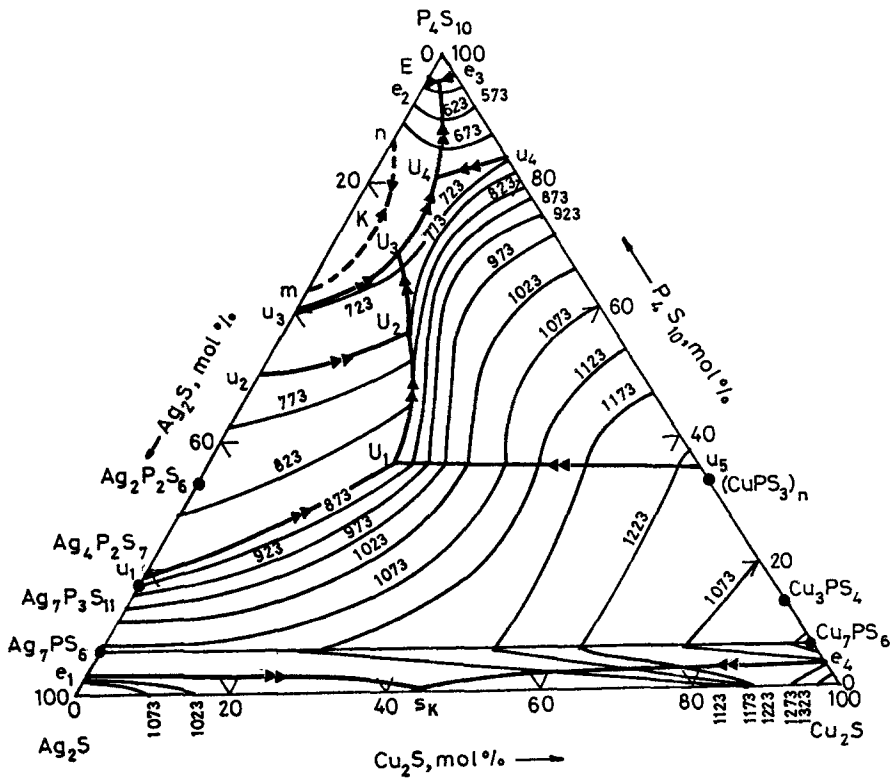

Fig. 3 Projection of the ternary system Ag_2S–Cu_2S–P_4S_{10} on the concentration triangle

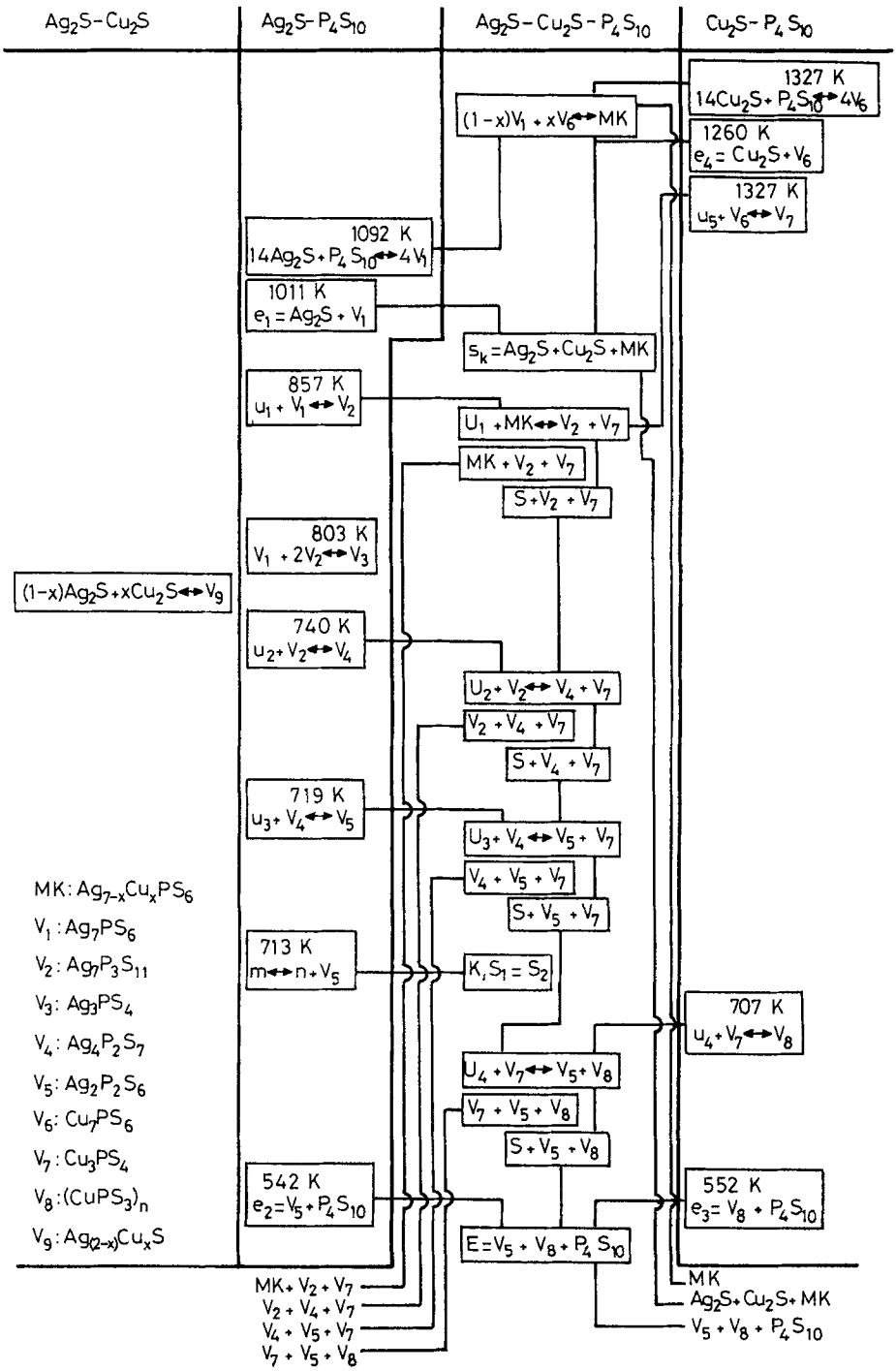

Fig. 4 Reaction pathways in Ag_2S–Cu_2S–P_4S_{10}

tinuously decreasing from the melting point of Cu_7PS_6 (1327 K) to that of Ag_7PS_6 (1092 K). Both components transform from a structure with the space group $P2_13$ to space group $F\bar{4}3$ m at relatively low temperatures. The transformation is shifted to even lower temperatures by addition of small amounts of either Cu or Ag to M_7PS_6. This transition temperature remains then nearly constant (487 K). X-ray data reveal that with increasing copper content the lattice constant and the cell volume are monotonicly decreasing (Fig. 6) in accordance with the size relation of Cu^+ and Ag^+ ions. We observed another region of complete solid solubility between the compounds Cu_3PS_4 and Ag_3PS_4, both crystallizing in the enargite type (space group $Pmn2_1$). Since both compounds decompose on heating, peritectically or peri- tectoidally respectively, the phase diagram is not a quasibinary cut. As in the case of the M_7PS_6 system the volume of the cell decreases nearly linear with increasing copper content. Surprisingly the lattice constants show a more complicated behaviour: a minimum in the lattice constant *b*

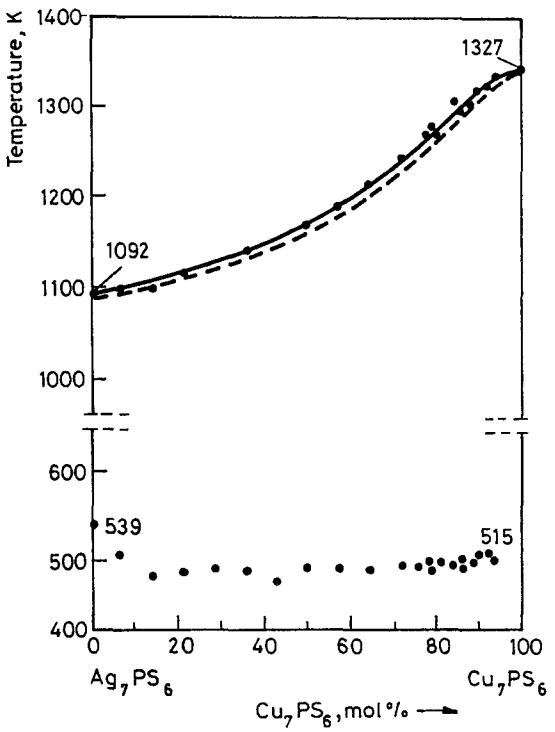

Fig. 5 The quasibinary section Ag_7PS_6–Cu_7PS_6

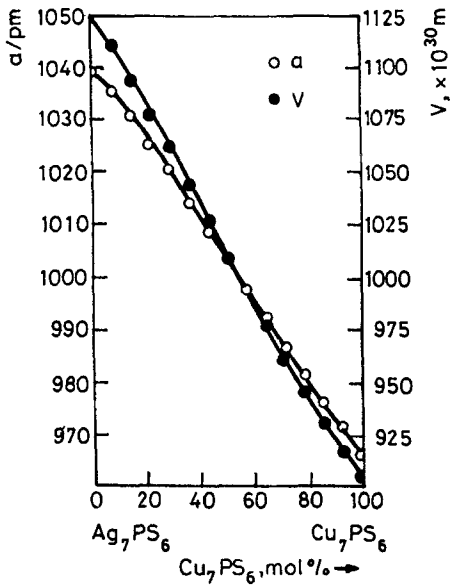

Fig. 6 Lattice constants and unit cell volumes in the system Ag_7PS_6–Cu_7PS_6

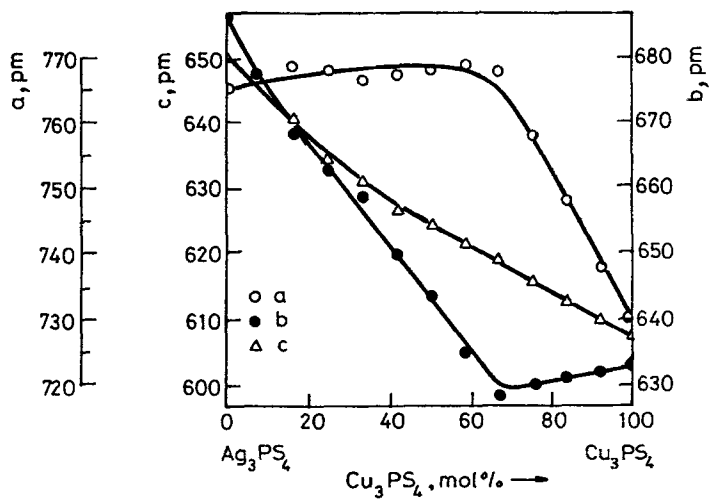

Fig. 7 Lattice constants in Ag_3PS_4–Cu_3PS_4

and a maximum of *a* is observed at approximately 25 mol% Cu (Fig. 7). This observation may indicate a possible superstructure of the solid solution with the composition $AgCu_2PS_4$.

* * *

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Zusammenfassung — Mittels DTA und Röntgendiffraktion wurde das quasiternäre System Ag_2S-Cu_2S-P_4O_{10} untersucht. Es konnte keine quasiternäre Verbindung gefunden werden. Erstmalig wurde das Phasendiagramm für das binäre Teilsystem Cu_2S - P_4O_{10} gegeben. Es enthält die Verbindungen Cu_7PS_6, Cu_3PS_4 und $(CuPS_3)_n$. Das unlängst beschriebene $Cu_4P_2S_7$ wurde nicht beobachtet. Thermoanalytische und röntgenografische Daten dieser Verbindungen werden gegeben. Die Verbindungen Cu_7PS_6 + Ag_7PS_6 und Cu_3PS_4 + Ag_3PS_4 sind im festen Aggregatzustand unbegrenzt mischbar.