The quasiternary system Ag$_2$S–Cu$_2$S–P$_4$S$_{10}$** was investigated by DTA- and X-ray measurements. No quasiternary compound was found. The phase diagram of the constituent binary Cu$_2$S–P$_4$S$_{10}$ is given for the first time. It contains the compounds Cu$_7$P$_6$, Cu$_3$P$_4$ and (CuP$_3$)$_n$. The previously reported Cu$_4$P$_2$S$_7$ was not observed. Thermal and X-ray data of these compounds are given. The compounds Cu$_7$P$_6$ + Ag$_7$P$_6$ and Cu$_3$P$_4$ + Ag$_3$P$_4$ are completely miscible in the solid state.

By the reaction of phosphorous chalcogenides with an excess 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 conditions under which such compounds are formed. One part of this series is the quasiternary system Ag$_2$S–Cu$_2$S–P$_4$S$_{10}$** reported in this work.

Silver or copper thiophosphates can be prepared by the reaction of metal sulphides or metal chlorides with P$_4$S$_{10}$ [1, 2] or by high-temperature synthesis from the constituent elements [3, 4]. The composition of the sample


** In the following the formula Cu$_2$S is given instead of Cu$_2$-δS, because its small deviations from integral stoichiometry have no influence on the phase diagram.
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$_2$S–Cu$_2$S–P$_4$S$_{10}$ system, obtained by DTA and X-ray investigations.

Experimental

High-purity elements (Cu: 99.999%, Degussa; Ag: 99.999%, Degussa; Cu: 99.999%, Vентрон; P: ultrapure, electronic grade, Hoechst AG, Werk Knap- sack; 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 (260 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). Automat- ed Diffractometer System (Stoe) Guinier–Simon FR 533 (Enraf Nonius) CuK$_{\alpha}$-radiation). X-ray data were evaluated by the program LSUCR [6].

Results

Data for the constituent binary systems

Ag$_2$S–Cu$_2$S was taken from Chang [7]. It is mainly based on the high temperature X-ray data of Skinner [8] and DTA measurements of Krestovn- nikow [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$_2$S–P$_4$S$_{10}$ [10] contains five compounds. The only congruently melting compound is Ag$_7$PS$_6$ with a melting point of 1092 K, and a