

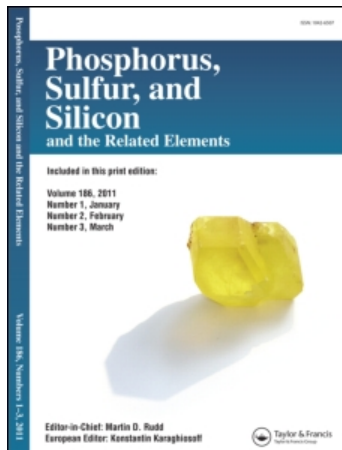
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Solid State Chemistry of A_4B_3 -Molecules

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SOLID STATE CHEMISTRY OF A_4B_3 -MOLECULES

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Abstract The system P_4S_3 - P_4Se_3 - As_4S_3 - As_4Se_3 was investigated by thermal and X-ray methods. Five regions of solid solubility with different crystal structures were found. All transform at higher temperatures into the plastically-crystalline state with β - P_4S_3 -structure.

The substituted species $P_{4-n}As_nS_{3-m}Se_m$ ($n = 0-4$, $m = 0-3$) are formed in molten mixtures of A_4B_3 -molecules (FIGURE 1). They were identified by HPLC and mass-spectrometric measurements.

After long equilibration times P_4Se_3 , As_4S_3 and As_4Se_3 decompose peritectoidally into the resp. A_4B_4 -species and an amorphous product.

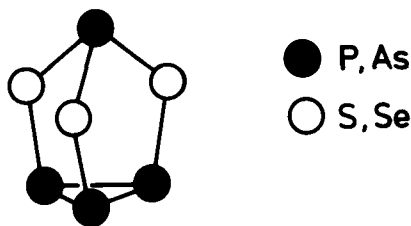


FIGURE 1 Structure of A_4B_3 -molecules.

THERMAL BEHAVIOUR

At higher temperatures the molecules P_4S_3 , P_4Se_3 , As_4S_3 , and with rapid heating rates As_4Se_3 , transform into a plastically-crystalline modification. Its structure is related to the β -Mn structure¹. The lattice constants of the

high-temperature phases were determined to $a = 1622.3(9)$, $c = 89.47(7)$ pm, 370 K, P_4Se_3 ; $a = 1660(1)$, $c = 87.86(15)$ pm, 450 K, As_4S_3 . $\beta-P_4S_3$ and $\beta-P_4Se_3$ transform within the plastically-crystalline state into a simple cubic structure. In high-temperature X-ray photographs a solid state reaction of P_4Se_3 , As_4S_3 and As_4Se_3 to P_4Se_4 , As_4S_4 resp. As_4Se_4 , and unidentified amorphous products was observed. The reaction rate increases in the order: $P_4Se_3 < As_4S_3 < As_4Se_3$. This peritectoid reaction determines the thermal behaviour of A_4B_3 compounds. At equilibrium conditions all, but P_4S_3 , decompose peritectoidally. Congruent melting, preceded by the transformation into the plastically-crystalline state, is observed only with fast heating rates. In the melt, however, the A_4B_3 molecules seem to be the stable species again.

Though most A_4B_3 molecules are metastable, we could obtain a "phase diagram" of the system P_4S_3 - P_4Se_3 - As_4Se_3 - As_4S_3 . Five regions of solid solubility with different crystal structures were found (FIG. 2).

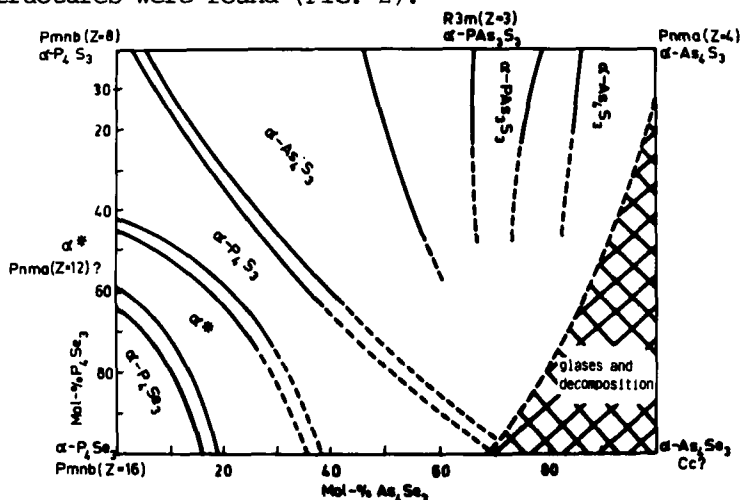


FIGURE 2 Phase regions in the system P_4S_3 - P_4Se_3 - As_4Se_3 - As_4S_3 (annealed at 400 K).

The homogeneity range of the different phases depends strongly on the annealing temperatures. All transform at higher temperatures into a plastically-crystalline modification with β - P_4S_3 structure.

Solid solutions in the system P_4S_3 - P_4Se_3 were obtained either by annealing P_4S_3 and P_4Se_3 in the plastically-crystalline phase or by melting the both components. In the first case the solid solution consists of P_4S_3 and P_4Se_3 , in the second case P_4S_2Se and P_4SSe_2 appear additionally. The properties of these mixed crystals of the same stoichiometry, but of different molecular composition, are very similar. Except for the thermodynamic data of the α - β transformation, no deviations of properties were observed.

HPLC-INVESTIGATIONS

Molecules of the type $P_nAs_{4-n}S_mSe_{3-m}$ can be prepared by melting mixtures of the A_4B_3 components. The existence of these molecules was verified by ^{31}P -NMR and mass-spectrometric measurements. The separation of the species was achieved by the HPLC method.

The concentration distribution of the different species in P_4Se_3 - As_4Se_3 , P_4S_3 - P_4Se_3 and P_4S_3 - As_4S_3 was determined and is given in FIG. 3 for the first system. The distribution in the other systems was published elsewhere².

In the first systems the distribution is statistical, whereas the PA_3S_3 is preferred in the system P_4S_3 - As_4S_3 .

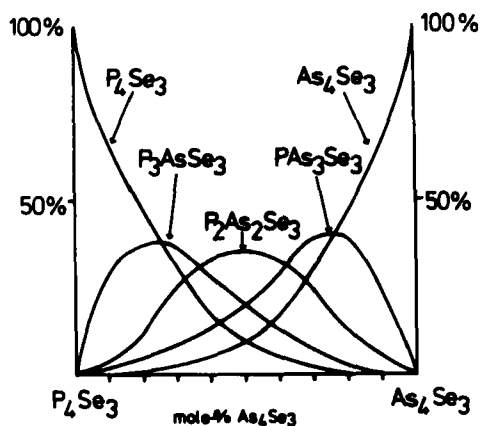


FIGURE 3 Concentration distribution in P_4Se_3 - As_4Se_3 .

NEW PHOSPHORUS CAGE MOLECULES

The preparation in the molten state, yielded further new molecules. The reaction of P_4S_3 with Sb_2S_3 leads to an antimony substituted A_4B_3 , i.e. P_3SbS_3 . P_4S_3 reacts with tellurium to P_4S_2Te .

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