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The compounds P_4S_3, P_4Se_3, As_4S_3 and As_4Se_3 and the quaternary system P_4S_3–P_4Se_3–As_4S_3–As_4Se_3

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Abstract

On heating, the compounds P_4S_3, P_4Se_3 and As_4S_3, and with rapid heating rates As_4Se_3, are transformed into the plastic crystalline β-modification, the structure of which is related to the β-Mn structure. This transition occurs in As_4S_3 and As_4Se_3 only under non-equilibrium conditions. P_4S_3 and P_4Se_3 show a phase transition within the plastic crystalline state, possibly in a cubic structure. The transformation temperature of P_4S_3 is very close to the melting point and can be observed only on cooling. The α–β transition shows a large hysteresis which is nearly independent of the cooling rate. In annealing experiments at elevated temperatures, As_4S_3 and As_4Se_3 decompose into As_4S_4 and As_4Se_4, respectively, and unidentified amorphous products.

The system P_4S_3–P_4Se_3 contains three regions of solid solubility, one from P_4S_3 to 45 mol% of P_4Se_3 with the α-P_4S_3 structure, the second from ≈48 to 60 mol% of P_4Se_3 with a new structural type (α^*-P_4S_3), and the third from ≈65 mol% of P_4Se_3 with the α-P_4Se_3 structure. On heating, all these phases transform into a plastic crystalline modification (β) with complete solid solubility between P_4S_3 and P_4Se_3. At higher temperatures this β-phase changes into the plastic γ-phase. The system P_4S_3–As_4S_3 reveals a broad metastable region of solid solubility, based on the structure of α-As_4S_3. All solid solutions undergo transformation into the plastic crystalline modifications at elevated temperatures. At ≈75 mol% of As_4S_3 a new structure is observed after equilibration at 390 K.

Crystalline samples of P_4Se_3–As_4Se_3 at ambient temperature show regions of solid solubility with α-P_4Se_3, α^*-P_4S_3 and α-P_4S_3 structure.

Solid solutions in the system P_4S_3–P_4Se_3 consist of molecules of the type $P_4S_nSe_{3-n}$ ($n = 0$–3) in statistical distribution, the formation being entropy controlled. In the mixtures of P_4S_3–As_4S_3, molecules of the type $P_{4-n}As_nS_3$ ($n = 1$–3), in which the occupation of the apical position for P atoms is favoured, were found. $P_{\mathrm{apical}}As_3S_3$ is the most stable of these isomers. The high abundance of $P_{\mathrm{apical}}As_3S_3$ reveals that the formation is enthalpy controlled. In the system P_4Se_3–As_4Se_3 a statistical distribution of substituted molecules was found.

The system P_4S_3–P_4Se_3–As_4S_3–As_4Se_3 shows five regions of solid solubility at room

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temperature. At all compositions these phases transform into the plastic crystalline β- and γ-modifications at higher temperature, forming a broad range of complete solid solubility. A decomposition reaction of the As_4B_3 molecules into As_4B_4 and amorphous products was observed in the As_4Se_3–As_4S_3 part of the system. The solid solutions in this system are formed from all possible isomers of the type $P_nAs_{4-n}S_mSe_{3-m}$ ($n = 0$–4, $m = 0$–3).

INTRODUCTION

During the investigation of the thermal properties of organic compounds, Timmermans [1] observed that some of these compounds were transformed below the melting point into a phase which had a high vapour pressure, plasticity and a very low entropy of fusion. He correlated this effect with the shape of the molecules, which were nearly globular, and named this group of compounds "cristaux plastique". Inorganic materials like white phosphorus and its derivatives P_4S_3 [2], P_4Se_3 [3], As_4S_3 [3] and As_4Se_3 [4] also crystallize in a plastic crystalline modification at elevated temperatures. These homologues were used to study the influence of solid solution and substitution on the transition into the plastic crystalline state by an investigation of the quaternary system P_4S_3–P_4Se_3–As_4S_3–As_4Se_3.

THE COMPONENTS

The structure of all A_4B_3 molecules (A = P, As; B = S, Se) is derived from an A_4 tetrahedron by insertion of bridging chalcogen atoms (B) into the three bonds of one A-atom at a corner to the equilateral triangle formed by the other three A atoms (Fig. 1). All bond lengths in this unit agree with the sum of the covalent radii of the atoms, thus indicating covalent bonding. The thermal stability of the A_4B_3 molecules differs. Thus, P_4S_3 is very stable. According to infrared and Raman spectra of solid, molten and gaseous P_4S_3, the molecular shape is preserved in all three phases [5]. Recent calculations of the stability of P_4S_3 by molecular dynamics simulations revealed, even at temperatures near 2000 K, no tendency of the P_4S_3 skeleton to break up or to isomerize [6]. In contrast, the As_4B_4 molecules undergo a decomposition reaction at elevated temperatures, in which As_4B_3 molecules are formed.

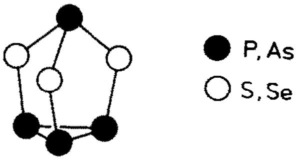

Fig. 1. Structure of the A_4B_3 molecule. A = ● (P, As); B = ○ (S, Se).

The crystallographic data of pure A_4B_3 compounds are summarized in Table 1. The normal crystalline modifications crystallize in the space group Pnmb or Pnma. The packing of the molecules roughly resembles

TABLE 1

Crystallographic data of the A_4B_3 modifications [a]

Compound	Space group	Lattice constants (pm)	Z	Ref.
α-P_4S_3	Pmnb	$a = 966.0(5)$; $967.0(3)$ $b = 1059.7(5)$; $1059.9(4)$ $c = 1367.1(5)$; $1367.8(3)$	8	7, 8
β-P_4S_3	R3 Plast. cryst.	$a = 1585$; $1580.9(5)$ $\alpha = 89.53°$; $89.54(1)$		3, 8
α-P_4Se_3	Pmnb	$a = 973.9(5)$ $b = 1179.7(6)$ $c = 2627.0(1.3)$	16	9
α'-P_4Se_3	Pnma	$a = 1099.7(3)$ $b = 984.5(3)$ $c = 1380.3(5)$	8	10
β-P_4Se_3	R3 Plast. cryst.	$a = 1622.3(9)$ $\alpha = 89.47°$		3
α-As_4S_3	Pnma	$a = 1124(2)$;$1121(2)$;$1121.4(2)$ $b = 990(3)$; $990(2)$; $991.6(3)$ $c = 656(2)$; $658(1)$; $659.8(3)$	4	11, 12, 13
α'-As_4S_3	Pnma	$a = 907$; $912(2)$ $b = 801$; $799(2)$ $c = 1030$; $1010(2)$	4	12, 14
β-As_4S_3	R3 Plast. cryst.	$a = 1660(1)$ $\alpha = 87.86(15)$		3
α-As_4Se_3	Cc or C2/c	$a = 2562(5)$ $b = 652(2)$ $c = 2301.5(5)$ $\beta = 123.6(4)°$	16	15
α'-As_4Se_3	Pnma	$a = 946(2)$ $b = 791(2)$ $c = 1041(2)$	4	15

[a] In order to give a consistent nomenclature of the different modification of A_4B_3 crystals, we use the symbol α for the rigid crystalline modification stable at ambient temperatures and α' for a rigid high temperature modification. The plastically crystalline modification which appears first is called β. The following plastically crystalline modification at higher temperatures is named γ. Thus, the sequence of phase transformations so far observed in A_4B_3 is represented as: $\alpha \rightarrow (\alpha') \rightarrow \beta \rightarrow (\gamma)$. The parentheses indicate that these forms are not observed in all A_4B_3 compounds.

that of hexagonal close packing; however, not all compounds are isotypic. The structures differ in the arrangement of the molecules on the symmetry planes of the structure and in the number of molecules in the unit cell. The non-bonded contacts agree reasonably with the sum of the van der Waals radii, indicating the absence of strong intermolecular bonds. Further refinement of the crystal structures of α- and α′-P_4Se_3 by Rollo et al. [10] showed that the structure of α-P_4Se_3 is an array of layers of double stranded helices lying in the *ab* plane. The strands are connected by weak intermolecular Se–Se bonds. In α′-P_4Se_3, which is isotypic with α-P_4S_3, the individual helices are retained but are no longer paired, which leads to a less efficient packing.

This situation, strong intramolecular and weak intermolecular bonds should influence the behaviour of A_4B_3 compounds during thermal expansion. The data for P_4S_3 [8] and P_4Se_3 [10] are well known. The bond lengths in the molecule do not change with temperature. The intermolecular distances, represented by the distances between the centres of gravity of the two independent molecules of the assymetric unit of P_4S_3, increase from 597.5 pm at 4 K to 605.5 pm at 309 K. The temperature dependence of the unit cell parameters shows that the changes in *b* and *c* for P_4S_3 and α-P_4Se_3 are similar. The change in *a* of α-P_4Se_3 is only about half that observed in the sulphide. This increase leads to a continuous weakening of the intermolecular bonds, which makes librations easier, although not excessive, because no pretransition phenomena are observed [16–18], and finally allows the α–β transformation, which is accompanied by an decrease in density of about 12% [8]. All plastic crystalline β-forms are isotypic [3], although the structure is not well known. The structures of the plastic modifications are of high symmetry, thus molecules of lower symmetry cannot be arranged in their lattice without disorder. May [19] assumed that in β-P_4Se_3 the centres of gravity of the A_4B_3 molecules are packed like the Mn atoms in the β-Mn type structure.

The enthalpies and entropies of the α–β transformation and the melting are given in Table 2. The data reveal that both the enthalpy and the entropy of the α–β transition are much larger than those of melting. The high entropies of transition can be interpreted in terms of orientational disordering occurring at the transition. Although the plastic crystals are sometimes called rotary phases, free rotation has never been observed in molecular crystals. In the plastic crystalline modifications, the molecules are trapped in potential wells, where they perform angular oscillations or librations and continuously reorient themselves around their centres of gravity under the restoring forces of their neighbours. The reorientations are frequent between 10^{-10} and 10^{-11} s^{-1} and restricted in number by the requirements of the symmetry elements of the space group of the crystal and the point group of the molecule. Guthrie and McCullough [20] proposed that the entropy change ΔS_{Tr} approximates to

TABLE 2

Thermal data of transitions in A_4B_3 compound

	P_4S_3	α-P_4Se_3	α'-P_4Se_3	As_4S_3	As_4Se_3
$T_{\alpha-\alpha'}$ (K)				404 [4] 422 [30]	
$\Delta H_{\alpha-\alpha'}$ (kJ mol^{-1})				≈1.0 [4] 1.44 ± −0.02 [25]	
$\Delta S_{\alpha-\alpha'}$ (kJ mol^{-1} K^{-1})				3.34 [30]	
$T_{\alpha-\beta}$ heating (K)	313.7 [25] 313.9 [2] 314 [4]	356 [4] 356 [28]	358 [10]	424 [4] 432 [30]	447 [4]
$\Delta H_{\alpha-\beta}$ heating (kJ mol^{-1})	10.35 ± 0.5 [25] 10.31 ± 0.05 [2] 9.75 ± 0.5 [4]	10.98 [4] 10.96 [28]	11.35 [10]	13.1 [4] 13.04 [30]	11.8 [4]
$\Delta S_{\alpha-\beta}$ heating (J mol^{-1} K^{-1})	33.0 ± 0.5 [25] 32.86 ± 0.15 [2]		31.7	30.8 [4] 30.2 [30]	26.5 [4]
$T_{\alpha-\beta}$ cooling (K)	259 [25]			391 [30]	
$\Delta H_{\alpha-\beta}$ cooling (kJ mol^{-1})	8.72 ± 0.4 [25]			13.90 ± 0.2 [30]	
$\Delta S_{\alpha-\beta}$ cooling (J mol^{-1} K^{-1})	33.67 ± 1.5 [25]				
	not observed in molten samples [10, 4]				
$T_{\beta-\gamma}$ heating (K)		479 [4]	480 [10]		
$\Delta H_{\beta-\gamma}$ heating (kJ mol^{-1})		1.3 [4]	1.30 [10]		
$\Delta S_{\beta-\gamma}$ heating (J mol^{-1} K^{-1})		2.71	2.71		
$T_{\beta-\mathrm{melt}}$ heating (K)	445 [4, 25]	522 [4]	517 [10]	484 [30] 491 [4]	
$\Delta H_{\beta-\mathrm{melt}}$ heating (kJ mol^{-1})	3.085 ± 0.05 [25] 3.08 ± 0.15 [4]	2.79 [4]	2.36 [10]	3.77 [4] 3.86 ± 0.04 [30]	
$\Delta S_{\beta-\mathrm{melt}}$ heating (J mol^{-1} K^{-1})	6.99 ± 0.1 [25]	5.34	4.56	8.00 [30, 4]	

$R \ln N_1/N_2$, where N_1/N_2 is the ratio of the number of molecular orientations in the high and low temperature phases [20], respectively. From this equation unreasonably high values were obtained for N_1 for many organic crystals and also for the A_4B_3 compounds. An alternative route was suggested by Clark et al. [21], who added an excess entropy to the Guthrie–McCullough contribution. This excess entropy could be correlated with the temperature range of the disordered phase and the molecular shape. The authors found a good correlation between the stability range of the plastic crystal and the difference in molecular parameters D_1 and D_2, which are chosen as the diameters of ellipsoidal molecules. A similar correlation exists for A_4B_3 molecules. It can be expressed by the equation [22]

$$D_2 - D_1 = -9.43 \times 10^{-4}(T_m - T_{tr}) + 0.33$$

For A_4B_3 molecules the maximum range ($D_2 - D_1 = 0$) is 350 K, which is in good accordance with a range of 370 K for organic molecules [21]. In

P_4Se_3 and As_4Se_3 a second plastic modification, the γ-phase, is observed. Its structure is still unknown but probably cubic.

The entropies of melting of plastic crystals are low. The entropy of melting can be separated into different contributions, arising from translational (trans), rotational or orientational (rot) or conformational (conf) disorder and to the volume change [23].

$$\Delta S_m = \Delta S_{trans} + \Delta S_{rot} + \Delta S_{conf} + \Delta S_{vol}$$

The entropies of melting of plastic crystals are reduced by the contribution ΔS_{rot} because this disorder is gained at the α–β transformation temperature. Their behaviour resembles that of rare gases, because in these there is no rotation contribution for spherical particles. For A_4B_3 molecules and white phosphorus P_4, the values are even lower than the gas constant R ($8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}$). Such small values occur for non-spherical molecules because their reorientational movements are connected with a translation of the centres of gravity, which increases the entropy of the plastic crystalline phase and thus decreases the ΔS_{trans} contribution of the entropy of melting [24]. The volume change on melting is approximately 2% [8]. This excess volume allows the translational disorder in the melt.

The thermal behaviour of the A_4B_3 molecules is complicated by hysteresis effects and decomposition reactions. During all cooling experiments an exothermic effect was observed in P_4S_3 between the freezing of the sample and the $\beta \rightarrow \alpha$ transformation. The sum of the enthalpies of this effect and that of the freezing equals the enthalpy of melting of P_4S_3. We assume that the primarily crystallizing phase of P_4S_3 has γ-P_4Se_3 structure. The additional exothermic effect in the DSC runs indicates the transformation of γ-P_4S_3 into β-P_4S_3, and the third one the β–α transition. In the β–α transformations of P_4S_3, P_4Se_3 and As_4S_3 strong hysteresis effects were observed. The α–β transition temperatures on heating (P_4S_3, 315 K; As_4S_3, 424 K) [3] and cooling (P_4S_3, 259 K; As_4S_3, 319 K) [3], differ, as reported also by Chattopadhyay et al. [25].

This hysteresis is nearly independent of the cooling rate. Wagner [26] explained this behaviour with the Gibbs energy curves of rigid and plastic phases. In Fig. 2 the Gibbs energy is given for various temperatures as a function of the parameter α

$$\alpha = \frac{n_{disordered}}{n_{total}}$$

where n is the number of molecules. At low temperature (T_1) this curve has one minimum 1, representing a state of the crystal where only a few molecules are disordered, i.e. the rigid crystalline state. In the plastic phase at high temperatures (T_5) the curve has again one minimum 5; in this case most of the molecules are disordered, but some are ordered because of cooperative effects. In the medium temperature ranges T_2, T_3

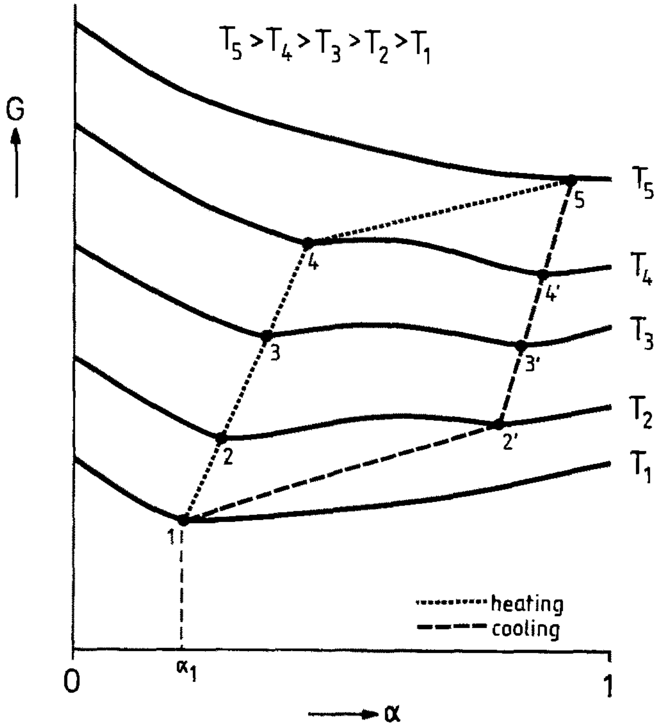

Fig. 2. Gibbs energy as function of the fraction of disordered molecules in a plastic crystal for different temperatures.

and T_4 the curve shows two minima, separated by a potential hill. When heating starts at state α_1 (1) the system passes the minima 2, 3, 4 and transforms into the plastic phase between T_4 and T_5. When this plastic crystal is cooled, the system goes down in the minima 4′, 3′, 2′ and undergoes a transition into the rigid modification at a much lower temperature between T_2 and T_1. This concept also explains the differences in transformation temperatures of A_4B_3 phases found in the literature. In a first heating experiment of P_4Se_3 we observed the α–β transition at 315 K, and on cooling it appeared at 259 K. In a second heating experiment, performed immediately, the α–β transformation was found at 309 K. After storing the sample for one day at room temperature the α–β transition was again observed at 315 K. Cooling the samples at different rates may thus produce different amounts of disordered regions in crystalline modification. With a higher degree of disorder the α–β transition is observed on reheating at lower temperatures; annealing restores the equilibration fraction of disordered molecules and gives the equilibrium α–β transition temperature. Fractional order in the plastic crystalline modifications is meanwhile established. Such static correlation of the individual molecules is due to two processes in the plastic phase.

(1) A reorientation of one molecule changes the reorientational probabilities of its neighbours;

(2) A molecular jump of a molecule triggers the jump of some of its neighbours in a preferred relative direction [27].

When P_4Se_3 is cooled from the melt to ambient temperature, the transitions melt→ γ-P_4Se_3→ β-P_4Se_3 are observed. The β–α transition is not found, even when the system is cooled to 250 K. The β-form is retained metastably at ambient temperature. It does not recrystallize within reasonable times, and hence the α–β transition is not observed in reheating experiments. Some doubts exist about the nature of this metastable β-P_4Se_3, because it is considered as a glassy crystal. In low temperature DSC runs, Rollo and Burns [28] observed a glass transition at 230 K. The Raman spectrum of quenched samples shows no lattice modes, and bands attributable to internal modes have smooth broad contours. The authors assume that orientational disorder is frozen and therefore none of the spectral features resulting from the interaction of molecules in a crystal are observed. Glassy crystals [29] have been observed for organic molecules. The disorder of the plastic phase is supercooled and finally goes into a glassy state, where the translational order of the plastic crystal is retained but the orientational disorder is frozen. However, C_p measurements of Chattopadhyay et al. [25, 30] on As_4Se_3 and P_4S_3 did not reveal "frozen in" states, therefore these authors exclude the glass-like state for these compounds.

The α–β–γ sequence of phase transitions occurs in As_4Se_3 and As_4Se_3 only on heating with fast rates. In the high-temperature X-ray photographs of As_4S_3 and As_4Se_3, reflections appeared which did not belong to the known A_4B_3 modifications. In As_4S_3 this phenomenon was previously described by Chattopadhyay et al. [30], who found in high temperature X-ray photographs above 438 K a phase with an unknown composition and structure. We could correlate these reflections to α-As_4S_4 and α-As_4Se_4 [3]. Thus, As_4S_3 and As_4S_3 decompose into As_4B_4 molecules and amorphous products. The melting point of As_4S_3 decreases with lower heating rates, because by this decomposition the melting point is depressed.

Previously we reported the decomposition of P_4Se_3 into P_4Se_4 at higher temperatures [3, 4], because in quenching experiments the X-ray pattern of α-P_4Se_4 was observed. The structure of this compound is not known. However, high temperature X-ray experiments revealed that the "α-P_4Se_4" X-ray pattern changes reversibly into that of β-P_4Se_3 at 320 K. Such reversibility was not observed in the As_4S_3 and As_4Se_3 decomposition. It is therefore doubtful that "α-P_4Se_4" contains P_4Se_4 molecules.

THE QUASIBINARY A_4B_3 SYSTEMS

At room temperatures, the system P_4S_3–P_4Se_3 [31] (Fig. 3) contains three broad regions of solid solubility, one between 0 and 42 mol% of

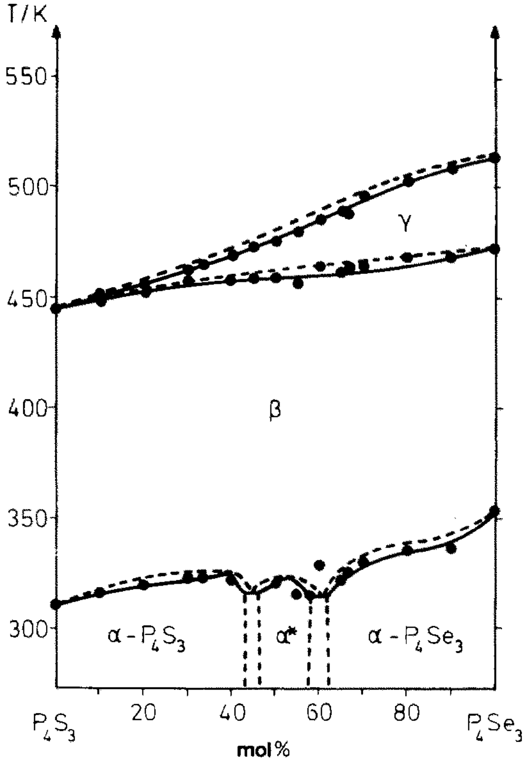

Fig. 3. The system P_4S_3–P_4Se_3.

P_4Se_3 with the structure of α-P_4S_3, a second from 48–58 mol% of P_4Se_3 with a new structure (α'-phase) and a third one from 62–100 mol% of P_4Se_3, based on the structure of α-P_4Se_3. On heating, these solid solutions transform into the plastic crystalline β-modification. Complete solid solubility between β-P_4S_3 and β-P_4Se_3 was found. Further increase of

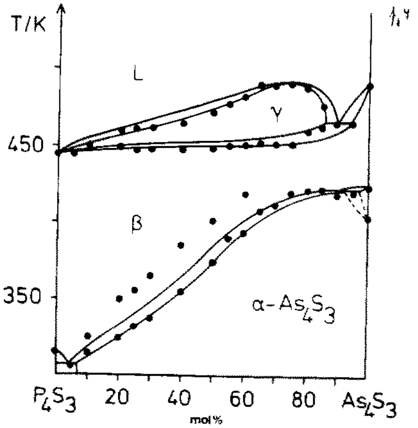

Fig. 4. The system P_4S_3–As_4S_3 annealed at 350 K.

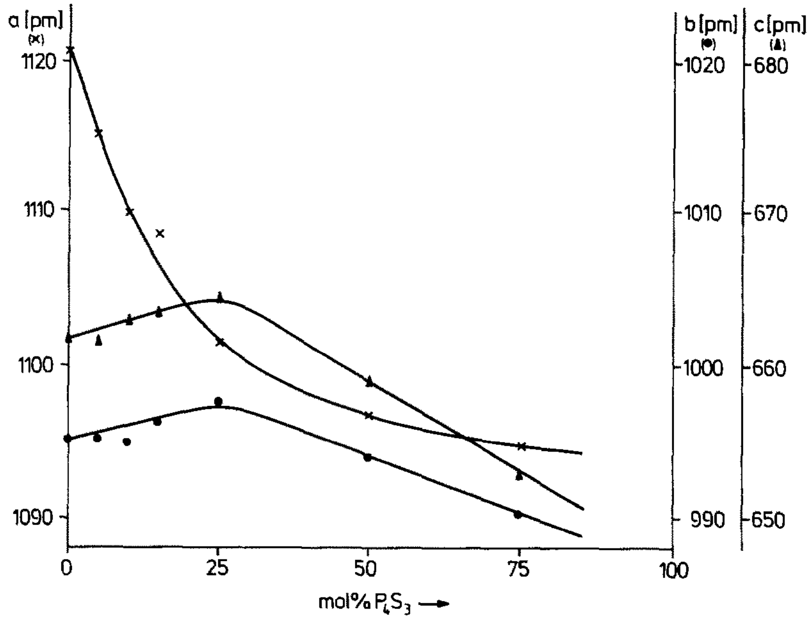

Fig. 5. The variation of the lattice parameters *a*, *b* and *c* of α-As_4S_3 solid solutions in the system P_4S_3–As_4S_3.

temperature changes the β-phase into the plastic crystalline γ-modifications.

The system P_4S_3–As_4S_3 [32] annealed at 350 K shows three solid phases (Fig. 4) at ambient temperature. The first one, a continuous series of solid solutions with α-As_4S_3 structure is found between $\approx$5 and 100 mol% of As_4S_3. The lattice constants of these α-A_4S_3 solid solutions are given in Fig. 5. The parameters *b* and *c* show small positive deviations from Vegards rule. The lattice constant *a* shows a strong negative deviation, with a maximum at 75 mol% of As_4S_3, which anticipates the formation of PAs_3S_3 at this composition. At higher temperature two further solid solutions were observed; one has the β-P_4S_3 structure and covers the whole system. The second plastic crystalline solid solution with γ-P_4Se_3 structure extends between 0 and $\approx$80 mol% of As_4S_3. Annealing at 390 K (Fig. 6) shows that some solid solutions are metastable. At 75 mol% of As_4S_3 a phase with a simple hexagonal structure (space group R3m, lattice constants $a = 987(2)$, $c = 931(6)$ pm [32]; $a = 986$, $c = 638.7$ pm [33]) splits the α-As_4S_3 solid solution in two parts. A preliminary structure determination [33] shows that this compound has a layer structure with the P_{apical} atoms at one side and the As atoms at the other side of the layer. This phase forms during annealing, because the mobility of the molecules increases at elevated temperatures, and enables them to move into the positions of this packing. At still higher temperatures the entropy effect

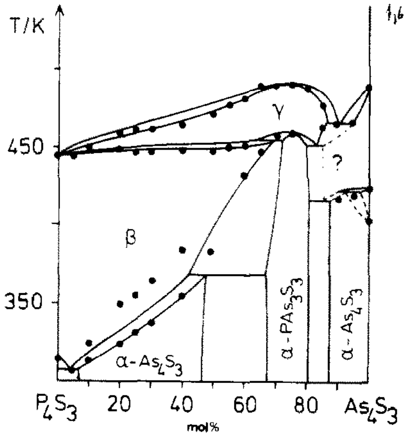

Fig. 6. The system P_4S_3–As_4S_3 annealed at 390 K.

dominates and the ordered PAs_3S_3 modification transforms into the plastic crystalline γ-P_4Se_3 structure, with disordered packing of the molecules. This behaviour resembles that of binary metal systems with super structures, e.g. Cu–Au. When a PAs_3S_3 melt is quenched, another metastable modification is observed. It crystallizes probably in the space group Pnma with the lattice parameters $a = 1071$, $b = 967$, $c = 716$ pm [32].

Investigations in the P_4Se_3–As_4Se_3 system [34] were difficult, because compositions with more than 20 mol% of As_4Se_3 solidify as glasses, which did not recrystallize even after long annealing periods. By sublimation, we were able to prepare in this region three crystalline samples with 32, 44 and 67 mol% of P_4Se_3. The compositions were determined by HPLC analysis of completely dissolved samples. The α-P_4S_3 structure was observed for the first two solid solutions, and the third one crystallized in the α-P_4Se_3 structure. This structural type was also found in a sample with 90 mol% of P_4Se_3, quenched from the melt and annealed at 370 K. Under the same conditions a sample with 80 mol% had the γ-P_4Se_3 structure, which after storing for four weeks at ambient temperature recrystallized into the α′-modification known from the P_4S_3–P_4Se_3 system.

The system A_4S_3–As_4Se_3 could not be investigated by thermal methods. All samples prepared from the melt consist mainly of A_4B_4 molecules [35].

SUBSTITUTION REACTIONS

X-ray and thermal methods are not suited to investigate the existence of isomers in the quaternary system. The element pairs P and As, S and Se belong to the same groups of the Periodic system. The replacement of bridging sulphur by selenium and phosphorus by arsenic should be possible. A recent report seemed to exclude the substitution of bridging

TABLE 3

A_4B_3 species in the system P_4S_3–P_4Se_3–As_4S_3–As_4Se_3

Binary	Ternary	Quaternary molecules [a]
P_4S_3	P_4S_2Se [b]	P_3AsS_2Se [c] (4I, of these 1 OP)
P_4Se_3	P_4SSe_2 [b]	P_3AsSSe_2 [c] (4I, of these 1 OP)
As_4S_3	As_4S_2Se [c]	$P_2As_2S_2Se$ [c] (6I, of these 2 OP)
As_4Se_3	As_4SSe_2 [c]	$P_2As_2SSe_2$ [c] (6I, of these 2 OP)
	P_3AsS_3 [b] (2I)	PAs_3S_2Se [c] (4I, of these 1 OP)
	$P_2As_2S_3$ [b] (2I)	PAs_3SSe_2 [c] (4I, of these 1 OP)
	PAs_3S_3 [b] (2I)	
	P_3AsSe_3 [b] (2I)	
	$P_2As_2Se_3$ [b] (2I)	
	PAs_3Se_3 [b] (2I)	

[a] I = isomers; OP = pair of enantiomers.
[b] Identified by MS, ^{31}P NMR and HPLC.
[c] Identified by MS.

atoms [36], whereas Leiva et al. [37] described the molecule $P_2As_2S_3$, therefore at least this kind of substitution should be possible. This fact encouraged us to investigate substitution reactions. In a series of experiments we found, by HPLC, ^{31}P NMR and mass spectroscopic measurements, that in the system P_4S_3–P_4Se_3–As_4S_3–As_4Se_3 all isomers of the general formula $P_{4-n}As_nS_{3-m}Se_m$ exist [38]. The quaternary system P_4S_3–P_4Se_3–As_4S_3–As_4Se_3 thus contains not only the A_4B_3 components, but 48 different molecules, which are listed in Table 3. Isomers (structural and optical) are possible for the same composition. As an example, in Fig. 7 all isomers with the molecular formula $P_2As_2S_2Se$ are depicted.

The concentrations of the different A_4B_3 species in the solid solutions were determined by HPLC experiments. In the reactions of the type

$$nA_4S_3 + (3-n)A_4Se_3 \rightarrow 3A_4S_nSe_{3-n} \qquad (A = P, As)$$

the number of bonds between A–A, A–S and A–Se does not change. If one assumes that the bond energies are independent of the type of molecule, the reaction should be entropy controlled, leading to a statistical distribution of the products. This assumption was realized experimentally by HPLC analysis. On the premise of ideal behaviour, the concentrations were used to calculate the equilibrium constants [39]

$$2P_4S_3 + P_4Se_3 \rightleftharpoons 3P_4S_2Se \qquad K_p = 32\ (\pm 15\%)$$

$$P_4S_3 + 2P_4Se_3 \rightleftharpoons 3P_4SSe_2 \qquad K_p = 23\ (\pm 15\%)$$

The values agree reasonably with those expected for a statistical distribution ($K_{p(stat)} = 27$). In the system P_4S_3–As_4S_3 the equilibrium constants for the following reactions were calculated from the concentrations deter-

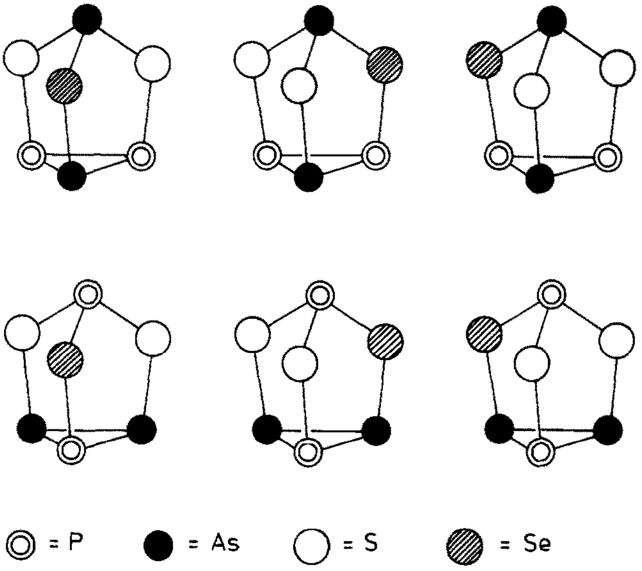

Fig. 7. Possible isomers of molecules with the empirical formula $P_2As_2S_2Se$.

mined by HPLC

$3P_4S_3 + As_4S_3 \rightleftharpoons 4P_3AsS_3$ $K_p = 120$ $(\pm 30\%)$

$2P_4S_3 + 2As_4S_3 \rightleftharpoons 4P_2As_2S_3$ $K_p = 1 \times 10^4$ $(\pm 20\%)$

$P_4S_3 + 3As_4S_3 \rightleftharpoons 4PAs_3S_3$ $K_p = 3.5 \times 10^5$ $(\pm 20\%)$

For each empirical formula two isomers, one with a phosphorus atom in the apex and the other with an arsenic atom, are possible. The isomers with a phosphorus atom at the apical position are preferred. The concentration distribution of the three substituted species is not statistical, $P_{\text{apical}}As_3S_3$ is abundant. This dominance can be explained thermodynamically. The P–S bond is more stable than the As–S bond. A phosphorus atom in the apical position allows more P–S bonds than an arsenic atom in the apical position. All reactions are therefore enthalpy controlled. Recently, Christian et al. [40] reported a structure determination of an α-As_4S_3 solid solution with 50 mol% of P_4S_3. They also observed similarly that phosphorus shows a preference for the apical site. The HPLC analyses of the system P_4Se_3–As_4Se_3 revealed a statistical distribution [38]. Recently the stability of all A_4B_3 molecules was calculated by Jones and Seifert [6]. They showed that the energy difference between the isomeric forms is the result of a compensation. The apical position of phosphorus is indeed favoured by the fact that the P–X bond is stronger, but counteracted by the transition from P–P to As–As or As–P bonds in the base, especially for PAs_3X_3 molecules. The latter effect dominates in Se, because of the smaller difference between the bond energies of PSe and AsSe, and therefore no preferential formation of isomers was observed in the selenide system.

High plasticity and self-diffusion rates reveal that plastic crystals are defective and the molecules are mobile. An additional feature of the plastically crystalline state is the cooperative nature of movements. NMR studies show that during rotational jumps at least one half of the nearest neighbour molecules must move simultaneously, which, in view of the close packing in the plastic phase, requires the rotational motion to be correlated. These molecular reorientations are connected with the comparative ease of diffusion known to prevail in plastic crystals, which requires a cooperation between the diffusing molecule and its neighbours [41].

Guided by these observations, we investigated the behaviour of powdered mixtures of P_4Se_3 and P_4Se_3 in the hope that an interaction between P_4S_3 and P_4Se_3 crystallites might occur. The samples were annealed at 373 K, i.e. both components were in the plastic crystalline β-phase. HPLC analysis revealed that at this temperature, at almost all concentrations, no substitution reactions of sulphur by selenium or vice versa occur. In P_4Se_3 rich mixtures only we found small amounts (less than 10%) of substituted molecules. However, by X-ray and thermal investigations of these samples, containing only P_4S_3 and P_4Se_3 molecules, we obtained solid solution structures, concentration ranges and transition temperatures equivalent to those for samples which were prepared from the melt. In the latter case the solid solutions consist of the species P_4S_3, P_4Se_3 and the substituted species P_4S_2Se and P_4SSe_2. The α–β transition temperatures are about 8 K higher and the entropies of the α–β transition are up to 10% higher than the values for the system prepared from the melt. Thermodynamically the substituted molecules can be considered as impurities. Similarly to the solid–liquid transition, these impurities decrease the transition temperatures and enthalpies. Their influence on the α–β transition is much larger than on the β–γ or γ–liquid transition, because the α–β transition consumes most of the energy which is needed to complete the series of phase transformations in these crystals.

THE QUATERNARY SYSTEM

The investigation of the quaternary system P_4S_3–P_4Se_3–As_4S_3–As_4Se_3 was seriously hampered by the tendency of the selenides to form glasses and of the As_4X_3 molecules to decompose at higher temperatures. The parts of the system which could be characterized by thermal and X-ray methods show broad regions of solid solubility, based on structures of the constituent components (Fig. 8). As an example for the complicated behaviour, the diagonal section P_4Se_3–As_4S_3 is given. The system behaves similarly to the system P_4S_3–As_4S_3. If one anneals at 350 K (Fig. 9a), at

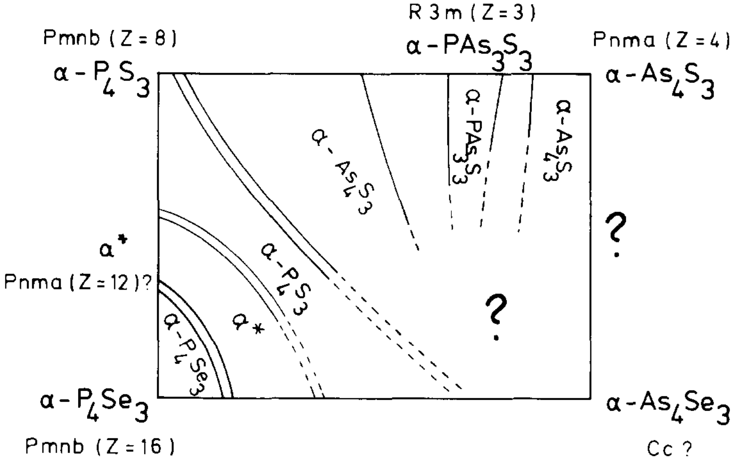

Fig. 8. Structure fields in the system P_4S_3–P_4Se_3–As_4S_3–As_4Se_3.

ambient temperature four regions of solid solubility exist, which transform at elevated temperatures first into the β- and then into the γ-phase. When annealed at 390 K (Fig 9b), the system shows a new solid solution based on the structure of $P_{apical}As_3S_3$, but the sequence of phases at higher temperatures does not change.

The lattice constants of some solid solutions in the quaternary system are given in Tables 4–6. The covalent radius of arsenic is ≈10% larger than that of phosphorus, and that of selenium ≈13% larger than that of sulphur. The cell volumes thus increase with a substitution of phosphorus by arsenic or selenium by sulphur. The lattice parameters *a* and *b* of

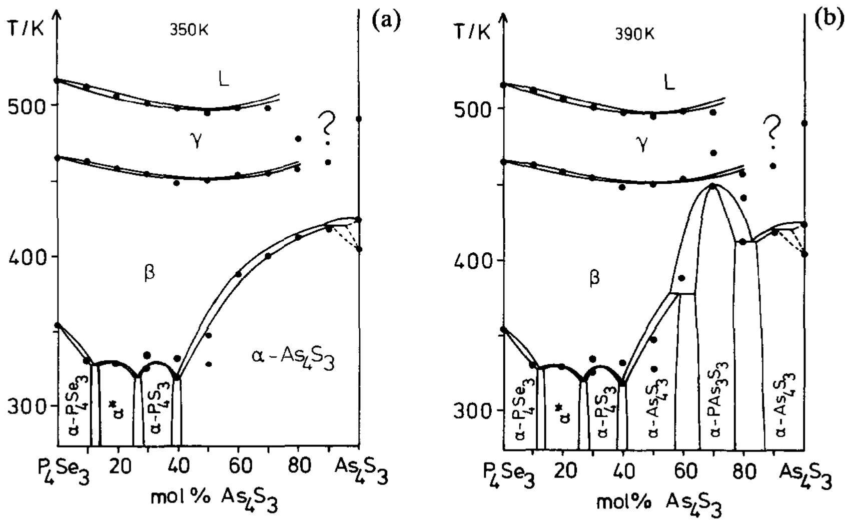

Fig. 9. The system P_4Se_3–As_4S_3: (a) annealed at 350 K; (b) annealed at 390 K.

TABLE 4

Lattice parameters of solid solutions in horizontal sections of the P_4S_3–P_4Se_3–As_4S_3–As_4Se_3 system

Mol.%	Structure	*a* (pm)	*b* (pm)	*c* (pm)	*V* (pm^3)
$P_4S_{1.5}Se_{1.5}:As_4S_{1.5}Se_{1.5}$					
100:0	α^*-P_4S_3	973.7	1141	1973	2.192×10^9
90:10	$\alpha^* + \alpha$				
80:20	α-P_4S_3	981.7	1082	1379	1.465×10^9
70:30	α-P_4S_3	992.5	1085	1377	1.483×10^9
60:40	α-As_4S_3	1115	1016	671	0.761×10^9
50:50	α-As_4S_3	1116	1017	671.0	0.762×10^9
40:60	α-As_4S_3	1119	1018	669.1	0.762×10^9
30:70	α-As_4S_3	1125	1019	666.6	0.764×10^9
20:80	α-As_4S_3	1126	1022	663.1	0.769×10^9
10:90	Amorphous				
0:100	Amorphous				
$P_4S_{1.05}Se_{1.95}:As_4S_{1.05}Se_{1.95}$					
100:0	α-P_4Se_3	973.2	1174	2607	2.979×10^9
90:10	α-P_4S_3	974.3	1087	1379	1.460×10^9
80:20	α-P_4S_3	987.3	1092	1378	1.486×10^9
70:30	α-P_4S_3	994.9	1101	1369	1.500×10^9
60:40	α-P_4S_3	999.8	1121	1360	1.524×10^9
50:50	α-P_4S_3	1007.0	1143	1351	1.555×10^9
40:60	α-As_4S_3	1143	1067	659.4	0.804×10^9
30:70	α-As_4S_3	1147	1068	654.2	0.801×10^9
20:80	Amorphous				
0:100	Amorphous				
$P_4S_{0.6}Se_{2.4}:As_4S_{0.6}Se_{2.4}$					
100:0	α-P_4Se_3	974.2	1170	2616	2.982×10^9
90:10	α-P_4Se_3	974.3	1179	2624	3.014×10^9
80:20	α-P_4S_3				
70:30	α-P_4S_3				
60:40	α-P_4S_3				
50:50	α-P_4S_3				
40:60	α-P_4S_3	1031	1176	1344	1.630×10^9
30:70	α-P_4S_3	1059	1199	1321	1.677×10^9
20:80	Amorphous				
0:100	Amorphous				

α-P_4S_3 based solid solutions increase with increasing arsenic content, whereas the lattice constant *c* decreases. Solid solutions with the α-As_4S_3 structure show a similar behaviour: the lattice parameters *a* and *b* increase with increasing arsenic and selenium content, whereas *c* decreases with increasing arsenic concentration. This may be explained by increased van der Waals interactions in the direction of the *c*-axis between arsenic-

TABLE 5

Lattice parameters of vertical sections of the system P_4S_3–P_4Se_3–As_4S_3–As_4Se_3

Mol.%	Structure	a (pm)	b (pm)	c (pm)	V (pm^3)
$P_2As_2S_3 : P_2As_2Se_3$					
100:0	α-As_4S_3	1089	1004	645.3	0.706×10^9
90:10	α-As_4S_3	1094	1006	652.2	0.718×10^9
80:20	α-As_4S_3	1101	1009	657.6	0.731×10^9
70:30	α-As_4S_3	1110	1012	659.5	0.741×10^9
60:40	α-As_4S_3	1112	1014	667.9	0.753×10^9
50:50	α-As_4S_3	1116	1017	671.0	0.762×10^9
40:60	α-As_4S_3	1122	1024	677.7	0.779×10^9
30:70	α-P_4S_3	1009	1145	1354.0	1.564×10^9
20:80	α-P_4S_3	1019	1149	1357.0	1.589×10^9
10:90	Amorphous				
0:100	Amorphous				
$PAs_3S_3 : PAs_3Se_3$					
100:0	α-PAs_3S_3	987.5		633.1	0.617×10^9
90:10	α-As_4S_3	1108	1003	655.2	0.728×10^9
80:20	α-As_4S_3	1110	1005	660.4	0.737×10^9
70:30	α-As_4S_3	1113	1012	662.3	0.746×10^9
60:40	α-As_4S_3	1120	1016	663.0	0.746×10^9
50:50	α-As_4S_3	1127	1019	664.4	0.763×10^9
40:60	α-As_4S_3				
30:70	Amorphous				
0:100	Amorphous				

containing molecules, which are also reflected by the increase in the α–β transition temperature with increasing arsenic content.

The number of molecules in the unit cell increases systematically from four in α-As_4S_3 to 16 in α-P_4Se_3. The increase reveals the tendency to form a close packing; in this way the molecules can occupy a more independent position in the unit cell, which also allows an optimum of intermolecular interactions. The α-PAs_3S_3 structure is limited to a small range and caused by the abundance of the $P_{apical}AsS_3$ molecule, which can build a layer type structure. The α*-structure may have its origin in the symmetry reduction of the A_4B_3 molecules by substitution. The pure A_4B_3 molecules are of C_{3v} symmetry, whereas substituted $P_4S_{3-n}Se_n$ molecules have the lower C_s symmetry. Further work needs to be performed in order to determine the new structures in this system and that of the high-temperature plastic γ-modification and to clarify the reasons for the appearance of the different structural types.

TABLE 6

Lattice parameters of diagonal sections of the system P_4S_3–P_4Se_3–As_4S_3–As_4Se_3

Mol.%	Structure	*a* (pm)	*b* (pm)	*c* (pm)	*V* (pm^3)
$P_4Se_3:As_4S_3$					
100:0	α-P_4Se_3	975.9	1181	2631	3.092 × 10^9
90:10	α-P_4Se_3	982.7	1183	2633	3.061 × 10^9
80:20	α-P_4S_3	1005	1092	1372	1.506 × 10^9
70:30	α-P_4S_3	999.6	1096	1374	1.505 × 10^9
60:40	α-P_4S_3 + α-As_4S_3				
50:50	α-As_4S_3	1118	1016	688.9	0.760 × 10^9
40:60	α-As_4S_3	1119	1012	668.9	0.756 × 10^9
30:70	α-As_4S_3	1112	1007	669.2	0.747 × 10^9
20:80	α-As_4S_3	1110	1005	660.4	0.737 × 10^9
10:90	α-As_4S_3	1112	1003	667.6	0.745 × 10^9
0:100	α-As_4S_3	1121	990.4	658.3	0.731 × 10^9
$P_4S_3:As_4Se_3$					
100:0	α-P_4S_3	966.0	1059	1367	1.398 × 10^9
90:10	α-As_4S_3	1098	993.2	652.0	0.711 × 10^9
80:20	α-As_4S_3	1102	998.7	656.2	0.722 × 10^9
70:30	α-As_4S_3	1106	1005	660.7	0.734 × 10^9
60:40	α-As_4S_3	1109	1010	664.3	0.744 × 10^9
50:50	α-As_4S_3	1116	1017	671.0	0.762 × 10^9
40:60	α-As_4S_3				
30:70	Two phases				
20:80	Amorphous				
0:100	Amorphous				

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