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THERMAL BEHAVIOUR OF A_4B_3 CAGE MOLECULES (A = P, As; B = S, Se)

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ABSTRACT

The thermal behaviour of A_4B_3 cage molecules (A = P, As; B = S, Se) was investigated by differential scanning calorimetry, X-ray methods and high-performance liquid chromatography. On heating, the molecules P_4S_3, P_4Se_3, As_4S_3, and with rapid heating rates As_4Se_3, transform into the plastic-crystalline state, the structure of which is related to the β-Mn structure with space group $R3m$. The lattice constants of the so far not described plastic crystals of P_4Se_3 and As_4S_3 were determined to be: $a = 1622.3(9)$ pm, $\alpha = 89.47(7)°$ at 370 K (P_4Se_3); $a = 1660(1)$ pm, $\alpha = 87.86(15)°$ at 450 K (As_4S_3). P_4S_3 and P_4Se_3 show a phase transition within the plastic-crystalline state, possibly in a simple cubic structure. The transformation temperature of P_4S_3 is very close to the melting point and can be observed only on cooling.

In the high-temperature X-ray photographs of P_4Se_3, As_4S_3 and As_4Se_3, the decomposition into P_4Se_4, As_4S_4 and As_4Se_4, respectively, and unidentified amorphous products were observed. This decomposition influences the melting behaviour of A_4B_3 compounds. At equilibrium conditions most decompose peritectoidally on heating, with fast heating rates, congruent melting or a transformation into the plastic-crystalline modification [As_4Se_3], occurs. In the melt, however, A_4B_3 seems to be the stable species again. The extent and the starting temperature of this decomposition was investigated; the decomposition, or polymerization, of the A_4B_3 molecules increased in the order: $P_4Se_3 < As_4S_3 < As_4Se_3$.

INTRODUCTION

The phase diagrams of P(As)–S(Se) mixtures contain molecular compounds of the type A_4B_3. These molecules have a structure which is derived from the P_4 tetrahedron by introducing three chalcogen atoms into the P–P bonds (Fig. 1). The crystal structures of these compounds at room temperature are well known (Table 1). Most of the α-phases crystallize in the same space group, they are not, however, isotypic.

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TABLE 1

Data of A_4B_3 structures stable at room temperature

Compound	Space group	Lattice constants	Z	Ref.
α-P_4S_3	*Pmnb*	$a = 966.0$ pm $b = 1059.7$ pm $c = 1367.1$ pm	8	1
α-P_4Se_3	*Pmnb*	$a = 973.9$ pm $b = 1179.7$ pm $c = 2627.0$ pm	16	2
α-As_4S_3	*Pnma*	$a = 1121$ pm $b = 990$ pm $c = 658$ pm	4	3
α-As_4Se_3	*Cc* or *C*2/*c*	$a = 2562.5$ pm $b = 652.2$ pm $c = 2301.5$ pm $\beta = 123.6°$ (or $\beta = 126.6°$)	16	4

The A_4B_3 molecules are of almost spherical shape; like other molecules of this type they transform at higher temperatures into the plastically crystalline state. Crystals in this state have relatively high vapour pressures, show a low entropy of fusion (usually < 21 J mol^{-1} K^{-1}), and are very soft and plastic.

In order to clarify the confusing nomenclature of the different modifications of A_4B_3 crystals, we name the normal crystalline modifications at low temperatures α; in the case when this modification transforms into a second normal crystalline modification at higher temperature, α is given a prime (α'). The first plastically crystalline modification is called β. A second plastically crystalline modification at still higher temperatures is named γ. The sequence of phase transformations so far observed in A_4B_3 crystals is thus $\alpha \rightarrow (\alpha') \rightarrow \beta \rightarrow (\gamma)$. Following this nomenclature the β-As_4S_3 and β-As_4Se_3 of Whitfield and co-workers [3,4] are named α in Table 1. Although these workers determined the space group and lattice constants of

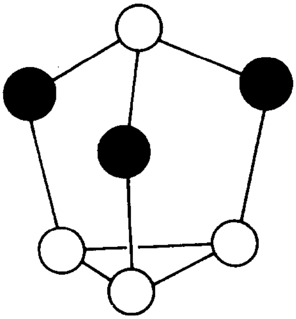

Fig. 1. Structure of A_4B_3 cage molecule, (○) P, As; (●) S, Se.

β-As_4Se_3, the observed reflections of our sample could not be correlated to the lattice parameters given in their work. Therefore, a list of *d*-values of our As_4Se_3 phase is given in Table 2.

Some recent work on P_4S_3, P_4Se_3, As_4S_3 and As_4Se_3 [5–9] enlightened the thermal behaviour of these molecules. In Table 3 some thermodynamic data are summarized. However, the thermal behaviour is still not understood. For this reason a thermal investigation of A_4B_3 molecules was carried out by means of differential scanning calorimetry (DSC), X-ray methods and high-performance liquid chromatography (HPLC).

EXPERIMENTAL

Preparation of the compounds

The four compounds were prepared by melting stoichiometric amounts of the corresponding pure elements: P(red), 99.999% (Knapsack); As, 99.995% (Preussag); S, 99.95% (Merck); and Se, 99.999% (Retorte), in evacuated, sealed quartz ampoules at ~ 700 K. The reaction products were then purified by extraction with CS_2. Additionally, As_4S_3 was sublimed on a tube cooled by liquid nitrogen; thus, As_4S_3 was obtained in the low-temperature

TABLE 2

d values and estimated intensities of reflections of α-As_4Se_3

d (pm)	623	575	566	535	530	513	488	480	430	385.4	377.5
I [a]	w	s	s	m	m	s	s	w	w	w	vw
d (pm)	356.9	330.3	329.0	325.9	324.4	321.0	318.1	315.8	311.6	308.4	
I [a]	vw	s	w	vw	vw	w	w	w	m	s	

[a] s, strong; m, medium; w, weak; vw, very weak.

TABLE 3

Thermal data of transitions in A_4B_3 compounds

Compound	*T* (K)	ΔH (kJ mol^{-1})	Type	Ref.
P_4S_3	314	9.75 10.35	$\alpha-\beta$	5,8
	445	3.08	β melt	
P_4Se_3	356	10.98	$\alpha-\beta$	5,7
	479	1.3	$\beta-\gamma$	
	522	2.79	γ melt	
As_4S_3	404/422	1.4	$\alpha-\alpha'$	6,8
	424/432	13.0	$\alpha'-\beta$	
	491	3.77 3.34	β melt	

modification. After melting, As_4Se_3 was a glass, which could not be transformed into the crystalline state by annealing. However, vacuum sublimation and extraction with CS_2 yielded crystalline products. P_4S_3 is bright yellow, As_4S_3 yellow, P_4Se_3 orange and As_4Se_3 red.

Experimental procedures

Thermal measurements were carried out by either a DSC-990 thermal analyzer (DuPont) or a DSC-2 (Perkin-Elmer) in closed aluminium pans. Usually, heating rates of 10 K min^{-1} were used. Differing heating rates are mentioned. The standard deviation of the given temperatures is ± 1 K.

X-ray photographs at ambient temperature were made by a Guinier-4 camera (Enraf-Nonius), at higher temperatures by a Guinier-Simon camera (type FR 533, Enraf-Nonius) with Cu-K_{α_1} radiation. SiO_2 was used as an internal standard.

HPLC measurements were carried out with a pump (type 64, Fa. Knauer). As stationary phase a column (length 30 cm, ID 4 mm) filled with LiChrosorb RP 18 (grain size 7 μm, Fa. Merck) was used, and as eluent a mixture of 90% methanol–10% water. The flow rate was 1 ml min^{-1}. The separated components were detected by UV absorption.

RESULTS

Normal crystalline high-temperature modifications

As_4S_3 occurs as a mineral in two forms, namely dimorphit II (α-As_4S_3) and dimorphit I (α'-As_4S_3). α-As_4S_3 is the room-temperature modification and transforms into α'-As_4S_3 at 404 K on heating at 10 K min^{-1} [6]. Bastow et al. [4] discussed two As_4Se_3 modifications. With the aid of high-temperature X-ray photographs we could show similar to the modifications of As_4S_3, that the β-As_4Se_3 of Bastow et al. is stable at room temperature. This phase transforms into α'-As_4Se_3 (α-As_4Se_3 of Bastow et al.) at 412 K on heating at 1.25 K min^{-1}. α'-As_4S_3 and α'-As_4Se_3 can be obtained in a metastable form at ambient temperature by quenching.

Plastically crystalline modifications

The structure of the plastically crystalline modification of P_4S_3 (β-P_4S_3), recently solved by Chattopadhyay et al. [10], is related to the β-Mn structure. The lattice parameters are: space group $R3m$; $a = 1585$ pm; $\alpha = 89°53'$; $Z = 20$. Our high-temperature X-ray photographs revealed the first plastically crystalline modifications of P_4Se_3 and As_4S_3 to be isotypic to β-P_4S_3. We determined the following lattice constants: for β-P_4Se_3; $a = 1622.3 \pm 0.9$

pm; $\alpha = 89.47 \pm 0.07°$ at 370 K; and for β-As_4S_3, $a = 1660 \pm 1$ pm; $\alpha = 87.86 \pm 0.15°$ at 450 K. The observed reflections of β-P_4Se_3 could not be correlated to the lattice constants of the cubic structure assumed by Monteil and Vincent [11].

Blachnik et al. [6] concluded from DSC-measurements that As_4Se_3 transforms into a plastically crystalline modification above 447 K. However, in high-temperature X-ray photographs of As_4Se_3 (heating rate 5 K h^{-1}) reflections due to a plastic phase were not observed.

P_4Se_3 shows a phase transition within the plastically crystalline state. At about 470 K a transformation of β-P_4Se_3 into γ-P_4Se_3 can be observed in high-temperature Guinier-Simon photographs; the list of reflections of γ-P_4Se_3 is given in Table 4. These values, determined during cooling experiments in the X-ray camera, differ from those given by Monteil and Vincent [11] for the γ-phase of P_4Se_3. γ-P_4Se_3 possibly crystallizes in a simple cubic structure like most plastic crystals.

DSC measurements revealed that a second plastically crystalline phase of P_4S_3 exists. In Fig. 2 the results of the DSC experiment on P_4S_3 are given. On heating, the expected large heat effect was observed, along with the α–β transition at 315 K and the smaller effect corresponding to the fusion of β-P_4S_3 at 445 K. During all cooling experiments a third exothermic effect was found, which lies between the peak due to the freezing of the sample and

TABLE 4

d values and intensities of γ-P_4Se_3

d (pm)	583	542	513	307	286	282
I [a]	s	m	vs	w	w	m

[a] vs, very strong; s, strong; m, medium; w, weak.

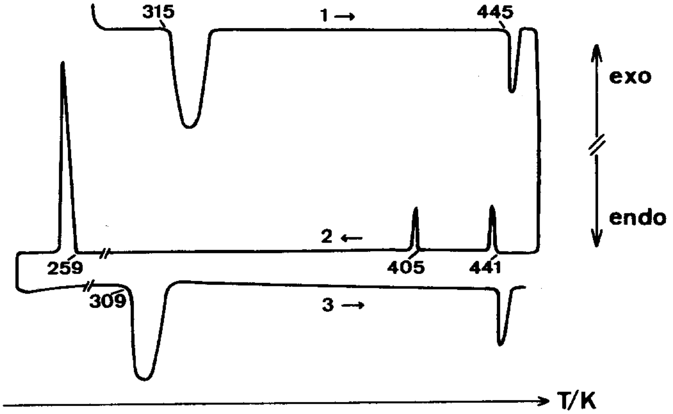

Fig. 2. Behaviour of P_4S_3 during heating and cooling experiments in the DSC. (1) First heating; (2) cooling; (3) second heating with hysteresis effect.

that caused by the $\beta \rightarrow \alpha$ transformation. The sum of the enthalpies of this new effect and of the freezing effect is nearly equal to the enthalpy of melting of P_4S_3, measured in the heating runs. An interpretation of this new thermal effect was possible by solving the phase diagram of the quasibinary system P_4S_3–P_4Se_3 [7], which revealed that a region of complete solid solubility based on γ-P_4Se_3 extends through the system from P_4Se_3 to pure P_4S_3. The measured effects, extrapolated to P_4S_3, show that the stability range of the γ-phase in P_4S_3 is very small. On cooling liquid P_4S_3, the primarily crystallizing phase, indicated by the first exothermic effect, has a γ-P_4Se_3 structure. The second exothermic effect in the DSC run indicates the transformation of this γ-P_4S_3 into β-P_4S_3. This behaviour is reproducible.

In the transformations of P_4S_3, P_4Se_3 and As_4S_3 different kinds of hysteresis effects were observed. As usual for the transformation into the plastic phase [12] the transition temperatures on heating (P_4S_3, 315 K; As_4S_3, 424 K) and on cooling (P_4S_3, 259 K [8]; As_4S_3, 319 K [9]), differ, as already reported by Chattopadhyay et al. [8,9]. An explanation of this anomaly was given by Wagner [13], who assumed a certain fraction of disordered molecules in the normal-crystalline phase and residual positional order in the plastic phase. This phenomenon leads to two transformation paths one on heating, the other on cooling. This assumption is supported by a second hysteresis of the α–β transformation of P_4S_3 and As_4S_3. The transformation temperature of annealed P_4S_3 is 315 K. In subsequent reheating DSC runs, however, the transition occurs at 309 K. A transition temperature of 315 K is again found after several hours storing at ambient temperature. Although Chattopadhyay et al. [8] found no residual entropy after the transformation of P_4S_3, we believe that this hysteresis effect is caused by orientationally disordered molecules in the α modification. The fraction of these molecules decreases to the equilibrium value by reorientational jumps, even at ambient temperature after several hours. Similar conclusions were drawn by Kolditz and Wahner [14], to explain their ^{31}P-NMR experiments. Though Gibby et al. [15] and Andrew et al. [16] assumed a rapid motion of the P_4S_3 molecule around the C_3 axis in the plastic phase, the movement must be cooperative, thus giving a certain amount of positional order. This is supported by the rapid diffusion in the plastic-crystalline state and by the structure of the β-phases of A_4B_3 molecules, which have no simple cubic or hexagonal lattice as usually found in the plastic phases. In P_4Se_3, a hysteresis comparable to this anomaly was observed. In the first heating experiment the α–β transformation is found at a higher temperature (474 K) than in subsequent runs (465 K). The difference between the transition temperature found by us and that reported by Monteil and Vincent [11] can probably be explained by this effect.

In experiments with P_4Se_3, differing hysteresis effects of the β–α transition were found. Instead of the very sharp peaks of the β–α transition of P_4S_3 and As_4S_3, in DSC cooling experiments with P_4Se_3, a broad peak between 300 and 270 K appeared. In a following heating experiment the peak indicating the α–β transformation splitted into two, a small one at 340 K and a large one at 350 K. Similar effects had been observed in P_4S_3/P_4Se_3 mixtures [7], and may be due to a two-step mechanism of the transition into the plastic phase.

The γ phases of P_4S_3 and P_4Se_3 could be undercooled. Contrary to the β–α transition the magnitude of the undercooling is dependent on the experimental conditions, and has no thermodynamic basis *.

Decomposition reactions

In the high-temperature X-ray photographs of P_4Se_3, As_4S_3 and As_4Se_3, reflections appeared which did not belong to the A_4B_3 modifications. In As_4S_3 this phenomenon was previously described by Chattopadhyay et al. [9], who found in high temperature X-ray photographs above 438 K a phase with an unknown composition and structure; this was stable at ambient temperature after cooling. We could correlate the additional reflections to the lattice parameters of As_4S_4 (in the photograph of Chattopadhyay the β, in ours the α modification) or α-P_4Se_4 and α-As_4Se_4 in the high-temperature X-ray photographs of P_4Se_3 and As_4Se_3. Thus, these compounds decompose peritectoidally into A_4B_4 molecules and unidentified amorphous products. The reflections of γ-P_4Se_3, reported by Monteil and Vincent [11], are also very similar to those of α-P_4Se_4. These decomposition reactions could be verified by annealing experiments. Samples of P_4Se_3, As_4S_3 and As_4Se_3 were annealed for a number of days at 500, 450 and 400 K, respectively; Guinier photographs of quenched samples showed only the reflections of α-P_4Se_4, α-As_4S_4, and α-As_4Se_4, respectively.

This decomposition influences the thermal behaviour of A_4B_3-compounds. The melting points of As_4S_3 vs. the heating rate are given in Table 5. The decrease in melting point with lower heating rates is due to a freezing point depression, caused by the formation of As_4S_4 molecules. A low heating rate allows the decomposition of larger amounts of As_4S_3, as compared with high heating rates. Similar observations were made for P_4Se_3. With heating rates of 10 K min^{-1}, P_4Se_3 and As_4S_3 melt congruently in the DSC at 516 and 491 K, respectively. In the case of P_4Se_3, this temperature can be reproduced in consecutive runs using identical heating rates. The melting temperature of As_4S_3 can be reproduced when the heating is stopped immediately after the melting process begins.

In the literature the melting process of P_4Se_3 is described as a borderline case between congruent melting and peritectical decomposition. According

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* In several DSC runs of A_4B_3 molecules exothermic effects between the α–β transformation and the melting point could be observed. Because these thermal effects were not exactly reproducible we are not able to give an explanation.

TABLE 5

Melting points of As_4S_3 vs. the heating rates

Heating rate (K min^{-1})	20	10	5	2	1	0.5
T_m (K)	487	485	482	480	476	474.5

to our measurements the melting behaviour is determined by the heating rate: at equilibrium conditions the compound decomposes peritectoidally, with fast heating rates it melts congruently.

The thermal behaviour of As_4Se_3 also depends on the heating rate. Some DSC runs, measured with different heating rates, are plotted in Fig. 3. The thermal effects could be interpreted from the X-ray data of quenched samples: in runs with heating rates of $\leqslant 5$ K min^{-1} the first thermal effect

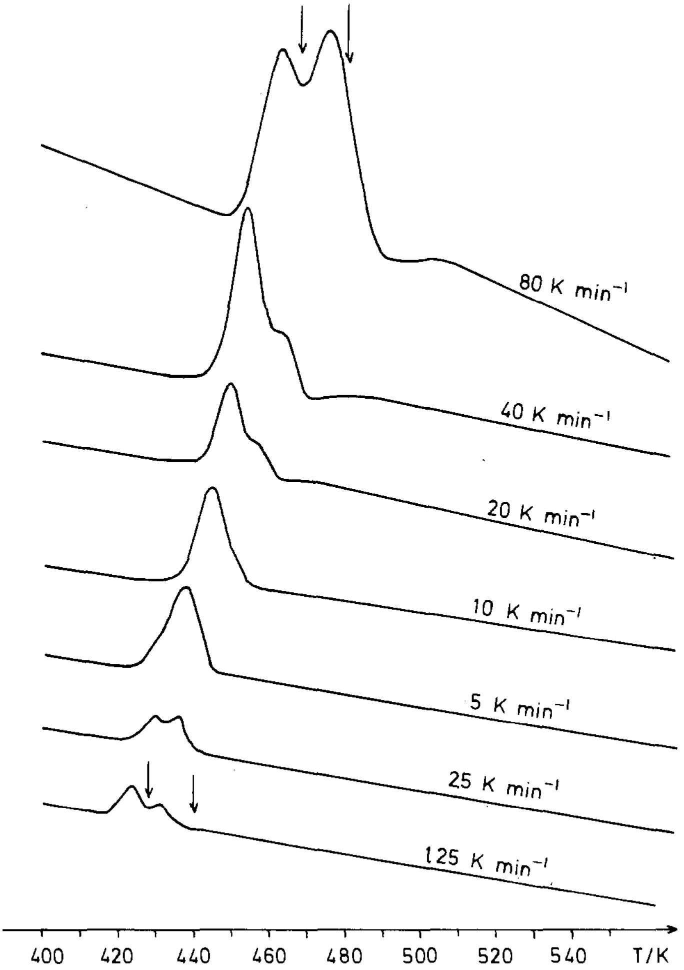

Fig. 3. DSC runs of As_4S_3 with different heating rates. (↓) samples for X-ray analysis quenched from these temperatures.

can be ascribed to the α–α' transition of As_4Se_3; the transition is not reversible. The second peak shows the decomposition of As_4Se_3 into an amorphous phase, which can be recognized by the absence of any X-ray reflections, the appearance of the sample, and a glass transition step in the DSC run at about 530 K. In contrast with the slow decomposition reactions of P_4Se_3 (As_4S_3) this phase transforms rapidly into the glassy state. After annealing, α-As_4Se_4 crystallizes from the glass. Between heating rates of 10 and 80 K min^{-1} the α–α' transition does not appear. In this DSC runs the first thermal effect is due to partial decomposition into the amorphous substance. The remaining crystalline parts transform into the plastically crystalline phase, indicated by the second peak. With increasing heating rates, the amount of As_4Se_3, transforming into the plastically crystalline phase increases. This is shown by the relationship between the peak areas and the respective peaks. In quenched samples the X-ray reflections of α- and α'-As_4Se_3, as well as some new reflections, could be detected. The latter were similar to those of the isotypical β phases of P_4S_3, P_4Se_3 and As_4S_3. We therefore assume that on fast heating As_4Se_3 can be transformed into a metastable, plastically crystalline phase of β-P_4S_3 structure.

HPLC investigations of the decomposition reactions of As_4S_3

The extent and the starting temperature of the decomposition reactions of As_4S_3 were investigated by HPLC measurements, which are much more sensitive for the detection of traces of As_4S_4 molecules than the X-ray technique. As_4S_3 and As_4S_4 can be separated on an RP 18 column with the eluent 90% methanol/10% water. The retention times are 7.8 min for As_4S_4 and 8.8 min for As_4S_3. The chromatographic experiments revealed that neither extraction with CS_2 nor sublimation yielded pure As_4S_3, but that As_4S_3 always contains traces of As_4S_4.

As_4S_3 samples were annealed at 400, 415 and 450 K for two weeks. In Table 6 the relationship between the areas of the As_4S_3 and As_4S_4 peaks in the HPLC chromatograms is given *. The results show that the decomposition starts at 400 K, i.e., in the normal crystalline modification, but that it is still not completed after annealing at 450 K for two weeks. The long reaction time explains why no thermal effects due to this reaction were observed in the DSC measurements. The decomposition of P_4Se_3 could not be investigated by HPLC experiments, because P_4Se_4 is insoluble in organic solvents. All techniques used gave strong evidence that, with the exception of P_4S_3, the A_4B_3 molecules decompose to the more stable A_4B_4 form by a solid-state reaction at higher temperatures.

In the melt, however, the A_4B_3 molecules seem to be the stable species

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* This relation does not give the quantitative composition of the samples directly, because no correction for the differing extinction coefficients was made (UV detection).

TABLE 6

Relationship between the ratio of the areas of the As_4S_3 and As_4S_4 peaks in HPLC chromatograms and the annealing temperature

T (K)	not annealed	400	415	450
$A_{As_4S_3}/A_{As_4S_4}$	37	33	22	1

again. This hypothesis is supported by several experimental observations.

(1) P_4Se_3, As_4S_3 and As_4Se_3 were prepared by melting stoichiometric amounts of the elements.

(2) Molten samples of P_4Se_3 and As_4S_3, already decomposed into the A_4B_4 phases in the solid state, showed, after melting on slow cooling in the high temperature X-ray camera as well as on X-ray photographs of quenched molten samples, the reflections of γ-P_4Se_3 and β-As_4S_3, respectively.

(3) Raman spectra gave evidence for the existence of As_4S_3 and P_4Se_3 molecules in the melt [17]. However, the concentration of both species in the melt cannot be derived from these data.

(4) A sample of P_4Se_3, annealed until the P_4Se_3 X-ray reflections vanished, was held in the melt at 580 K for a number of minutes and then cooled to low temperatures (liquid N_2). The following DSC run showed an exothermic peak at 481 K and then the melting point of pure P_4Se_3. A sample of the same substance which was annealed for 20 h in the solid state at 500 K does not show the thermal effects of pure P_4Se_3, instead, an exothermic effect at 566 K, well above the melting temperature of P_4Se_3, was present. This effect is probably due to the reforming of P_4Se_3 molecules.

DISCUSSION

According to Kitaigorodskiis theory, molecules are packed to make the best use of the available space: "the protrusions of one molecule will pack into the hollows of the next" [18]. The number of contacting molecules is usually twelve, with the structure assumed to be built from close-packed layers of molecules. It could be expected that molecules with the same symmetry and the same molecular structure should crystallize in the same structure, however, α-P_4S_3, α-P_4Se_3, α-As_4S_3 and α'-As_4Se_3 crystallize in similar but not isotypical structures. We assume that a variation in the intermolecular interactions leads to the different crystal structures. On transformation into the plastically crystalline phase there is a drastic increase in molar volume, in the case of P_4S_3 this is about 12% [8]. Thus, in the plastically crystalline phase, the molecules are not packed closely. They are rather arranged in such a way that the sterical restrictions for an orientational disordering are minimized. The small chemical and size differences of the individual compounds become insignificant and all compounds crystallize in the β-P_4S_3 structure. The similarity of all α–β transitions can also be shown by an analysis of the transition entropies according to Guthrie and McCullough [19] who used values of the entropies of transition to estimate the number of distinguishable molecular orientations in the plastic phase, by the formula

$$\Delta S_{\alpha-\beta} = R \ln N_{\text{plast}}/N_{\text{cryst}}$$

The relation $N_{\text{plast}}/N_{\text{cryst}}$ is very similar in all A_4B_3 molecules, approximately 40–43, however, the measured enthalpies of transition are much higher than could be expected from the symmetries of the molecules and the lattice. The dependence of the plastically crystalline range on the deviation from globular shape first reported by Clark et al. [20], was also observed for A_4B_3 molecules (60 K, As_4S_3; 143 K, P_4Se_3).

The very small entropies of fusion, which are $< R$ for P_4Se_3 and P_4S_3 can be explained by a theory of Aston et al. [21]. They found that in molecules with shapes deviating from the ideal spherical form, the rotation leads to a translation of the centre of gravity. This translation results in an increase in the entropy of the plastic phase and a decrease in ΔS_f.

The thermal stability with respect to the decomposition or polymerisation of the β-phase decreases in the order $P_4S_3 > P_4Se_3 > As_4S_3 > As_4Se_3$. β-P_4S_3 is a thermodynamically stable phase. β-P_4Se_3 is stable only at lower temperatures and decomposes peritectoidally into P_4Se_4 at higher temperatures ($>$ 450 K). β-As_4S_3 can only be obtained in a metastable form. β-As_4Se_3 is only formed metastably in a very small temperature range for short periods.

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