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Solid State Studies on Synthetic and Natural Crystalline Arsenic(III) Sulfide, As_2S_3 (Orpiment): New Data for an Old Compound

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Synthetic monoclinic orpiment was recrystallized by annealing the glass at 523 K for 1 year. The apparent heat of fusion of orpiment at $T_{\mathrm{fus}} = 601$ K (onset) was found to depend linearly on the ratio V/m (V = inner volume of the sample pan, m = in-pan sample mass) because of partial sublimation. This gives $\Delta_{\mathrm{fus}}H = 131$ J g^{-1} if $V/m = 0$ and the specific volume of the vapor phase $\upsilon(\mathrm{v}) = 190$ cm^3 g^{-1} if $\Delta_{\mathrm{fus}}H = 0$ at the conditions of the orpiment−liquid−vapor triple point. Lattice parameters of orpiment and liquid density were measured in the 283−393 K and 750−1250 K ranges, respectively. Subsequent specific volume values were used to calculate the slope dp/dT (≈53 MPa K^{-1}) for the orpiment−liquid equilibrium curve of the As_2S_3 $p-T$ diagram.

1. Introduction

The naturally occurring crystalline arsenic(III) sulfide, As_2S_3, has been known from antiquity as orpiment. However, production of synthetic crystalline samples through direct synthesis from the elements usually yields a vitreous solid that is notoriously difficult to crystallize, even after seeding the melt.[1] Nevertheless, crystals had already been obtained by annealing the glass for 12 days at 573 K[2] or 7 days at 568 K,[3] while transport through the vapor phase under a temperature gradient is known to produce heterogeneous mixtures made of realgar As_2S_2 and orpiment crystals together with a glassy deposit.[4]

As_2S_3 is an important material for physical (semiconducting, optical) applications and, because it is an excellent glass former, basic thermodynamic properties (melting point, heat of fusion, etc.) have been obtained from natural rather than synthetic samples. The purity of natural orpiment was questioned by Cernosek et al.[3] who found that synthetic orpiment melts at $T_{\mathrm{fus}} = 580$ K with a melting enthalpy ($\Delta_{\mathrm{fus}}H$) of 78 J g^{-1}, instead of 122 J g^{-1} as previously reported by Blachnick.[5] In addition, an endothermic effect (9.75 J g^{-1}) was observed at 443−447 K[6] and related to a reversible transformation of orpiment (thus named form II) into another form (form I). Tonkov[7] reported that the enthalpy change for this transition equals 14.63 J g^{-1} and that form I melts at 580 K with $\Delta_{\mathrm{fus}}H(\mathrm{I}) = 116.7$ J g^{-1}. It is to be noticed that the existence of another form of As_2S_3 (form β) is mentioned in Pascal's treatise,[8] in which it can be read that, according to experiments by Borodowski in 1906, this form appears at 540 K, and its density (3.252 cm^3 g^{-1} at 292 K) is smaller than that (3.502 cm^3 g^{-1} at 292 K) of orpiment. However, Besson et al.[9] and Devaud et al.[10] observed no transition of orpiment into any other form and reported that orpiment melts at about 577 K at ordinary pressure and crystallizes from the melt under pressure and temperature.

Because contradictory information as to the thermal behavior and heat of fusion of crystalline As_2S_3 is found in the literature (see Table 1), recrystallization experiments and subsequent heat of fusion measurements were performed together with measurements of densities of solid and liquid synthetic As_2S_3 as a function of the temperature.

Results are presented and discussed in the following.

2. Materials and Methods

Synthetic As_2S_3 was prepared by mixing stoichiometric amounts of sulfur and arsenic in evacuated silica tubes. Sulfur crystals were crushed into small pieces, and arsenic was sublimed twice under a vacuum. Shiny metallic-grey crystalline pieces of arsenic were cut and used without grinding. The mixture was heated to about 1000 K, and after 1 week, molten As_2S_3 was slowly cooled to room temperature; as usual, a glass was obtained. Part of this glass was transferred into another silica tube which, after sealing under a

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(1) Voigt, B.; Jacob, B. *Monatsh. Chem.* **1982**, *113*, 895.
(2) Yang, C. Y.; Paesler, M. A.; Sayers, D. E. *Mater. Lett.* **1986**, *4*, 233.
(3) Cernosek, Z.; Cernoskova, E.; Benes, L. *Mater. Lett.* **1999**, *38*, 336.
(4) Bowlt, C.; Ghosh, B. N. *Br. J. Appl. Phys.* **1965**, *16*, 1762.
(5) Blachnik, R.; Hoppe, A.; Wickel, U. *Z. Anorg. Allg. Chem.* **1980**, *463*, 78.
(6) Kirkinskii, V. A.; Ryaposov, A. P.; Yakushev, V. G. *Izv. Akad. Nauk SSSR, Neorg. Mater.* **1967**, *3*, 1931.
(7) Tonkov, E. Y. *High Pressure Phase Transformations, A Handbook*; Gordon and Breach: Langhorne, PA, 1992; Vol. 1.
(8) Pascal, P. *Nouveau Traité de Chimie Minérale*; Masson: Paris, 1958; Vol. 11.
(9) Besson, J. M.; Cernogora, J.; Zallen, R. *Phys. Rev. B* **1980**, *22*, 3866.
(10) Devaud, G.; Aziz, M. J.; Turnbull, D. *J. Non-Cryst. Solids* **1989**, *109*, 121.

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Table 1. Temperature (T_{fus}) and Heat of Fusion ($\Delta_{Fus}H$) for Crystalline As_2S_3 from the Literature[a]

T_{fus} (K)	$\Delta_{fus}H$ at T_{fus} (kJ mol^{-1})	$\Delta_{fus}H$ at T_{fus} (kcal mol^{-1})	$\Delta_{fus}H$ at T_{fus} (J g^{-1})	$\Delta_{fus}H$ at 298 K (kJ mol^{-1})	ref
599					1
580			**78**		3
581	**30.05**		*122.14*		5
583	**28.7** (form I)		*116.65* (form I)		7
577					9, 10
583					11, 12
581			**122.09**		13
585		**6.85**	*116.49*		14
		4.5 ± 2.0	*76.5 ± 34.0*		15
				23.33 (*94.83 J g^{-1}*)	16

[a] Bold: original values given by the authors. Italic: values calculated from original values, taking $M(As_2S_3) = 246.032$ g mol^{-1} and 1 cal = 4.184 J.

vacuum, was left for standing at 523 K for 1 year. It is to be noticed that the tubes were maintained vertically during synthesis and annealing, so as to keep the top of the tubes at a temperature greater than that of the bottom, thus preventing incongruent condensation of the vapor.

For the sake of comparison, samples of natural orpiment were taken from the mineral collections of the faculty of geology of the University of Barcelona (sample B) and the Faculty of Pharmacy of Paris (sample P). In both cases, shiny lamellar yellow crystals were extracted from the core of blocks whose dimensions were about 2 × 3 × 4 cm.

Elemental analyses and scanning electron microscopy (SEM) photographs were obtained by using an Oxford energy-dispersive X-ray spectrometer linked to a JEOL JSM-6400 scanning electron microscope.

An X-ray powder diffraction (XRPD) profile was recorded at 295 K from a crushed aliquot introduced into a Lindemann capillary (0.5 mm diameter), using a high-resolution INEL diffractometer equipped with a CPS120 position-sensitive multidetector (Debye−Scherrer geometry, transmission mode, Co Kα_1 radiation (λ = 1.7889 Å)).

XRPD data collection as a function of temperature from powder placed on a silicon plate was carried out under nitrogen flow with a PanAlytical X'pert Pro diffractometer (parafocusing Bragg−Brentano (θ-2θ)-type geometry coupled with an X'Celerator detector) equipped with an Anton-Paar TTK heating chamber. The Cu Kα_1 radiation (λ = 1.5406 Å) was selected by means of a Johansson-type monochromator. Data were collected isothermally at 10 K intervals in the 283−393 K range, at a heating rate between data collection of 3 K·min^{-1}.

The room-temperature lattice parameters previously found were used as a starting point for iterative Pawley refinements[17] of the XRPD profiles.

Samples subjected to differential scanning calorimetry (DSC) consisted of single crystals and small crystalline pieces picked under an optical microscope and introduced in aluminum pans subsequently sealed with covers of the same metal. Experiments were run at a 5 K min^{-1} rate with the DSC cell of a Mettler DSC822^e analyzer, and other analyzers (TA2000 and TA-2920-MDSC, both from TA-Instruments) were used for comparison purposes.

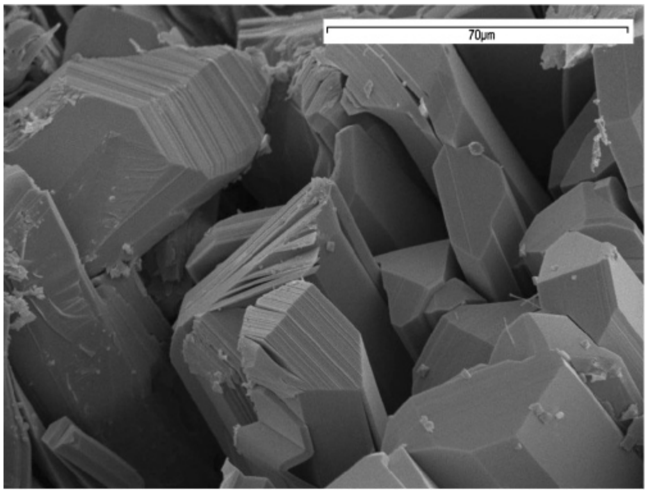

Figure 1. SEM photograph of crystals of synthetic orpiment grown from the glass during 1 year of annealing at 523 K. Accelerating voltage: 15 kV. Horizontal bar: 70 μm.

Liquid density measurements at different temperatures were performed as follows: a calibrated cylindrical silica tube (1 mm thick), whose inner diameter (9.516 ± 0.004 mm) was measured by means of an alesometer sensitive to 0.001 mm, was filled with 13.428 ± 0.004 g of glassy As_2S_3, then sealed under a vacuum. Afterward the tube was suspended vertically in the central part of a movable cylindrical furnace (50 cm high) and allowed to equilibrate at a fixed temperature. The height of the melt was determined by means of a cathetometer sensitive to 2 μm within about 10 s just after the furnace was temporarily moved upward.

It is worth noting that although the silica glass also expands as the temperature increases, no correction was applied because silica expansion has proven negligible in the T range under consideration.[18]

3. Results

A SEM photograph of lemon-yellow As_2S_3 crystals grown during a 1-year annealing of the glass is shown in Figure 1, in which stacked sheets, reminiscent of a layered structure, can be observed.

Elemental analyses showed that the composition of the two natural samples is virtually the same as the ideal composition of the synthetic crystals. At most, traces of copper could be guessed in the orpiment sample from the deposit of the University of Barcelona (sample B).

The experimental XRPD profile at 295 K is shown in Figure 2 together with the profile calculated using the atomic coordinates found by Mullen and Nowacki.[19] It can be seen that the two profiles agree with each other. In addition, the lattice parameters were refined from 46 reflections by means of the UnitCell software.[20] The parameter values given in Table 2 are close to the values reported in the literature.

The DSC results (temperature and heat of fusion values) are compiled in Table 3, and typical DSC curves are shown in Figure 3.

The glass transition (475 < T_g, K (midpoint) < 479) was found to occur within 466−471 K (onset) and 478−482 K (end) after heating again, at a 5 K min^{-1} rate, and synthetic

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(11) Jonker, W. P. A. *Z. Anorg. Chem.* **1909**, *62*, 89.
(12) Dembovskii, A.; Polyakov, Y. A.; Vaipolin, A. A. *Izv. Akad. Nauk SSSR, Neorg. Mater.* **1968**, *4*, 767.
(13) Blachnik, R.; Hoppe, A. *J. Non-Cryst. Solids* **1979**, *34*, 191.
(14) Myers, M. B.; Felty, E. J. *J. Electrochem. Soc.* **1970**, *117*, 818.
(15) Mills, K. C. *Thermodynamic data for inorganic sulphides, selenides and tellurides*; Butterworths: London, 1970.
(16) Bryndzia, L. T.; Kleppa, O. J. *J. Chem. Thermodyn.* **1988**, *20*, 755.
(17) Pawley. G. S. *J. Appl. Crystallogr.* **1981**, *14*, 357.
(18) Brückner, R. *J. Non-Cryst. Solids* **1970**, *5*, 123.
(19) Mullen, D. J. E.; Nowacki, W. *Z. Kristallogr.* **1972**, *136*, 48.
(20) Holland, T. J. B.; Redfern, S. A. T. *Mineralog. Mag.* **1977**, *61*, 65.

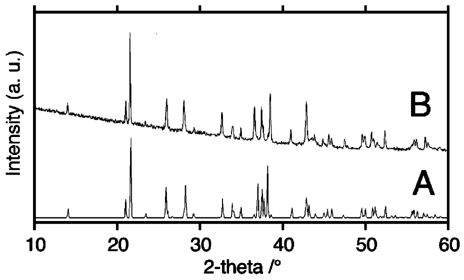

Figure 2. Synthetic orpiment. High-resolution XRPD profile at 295 K. (A) Calculated using lattice parameters, space group, and atom coordinates from ref 19. (B) Experimental, $\lambda(\text{Co K}\alpha_1) = 1.7889$ Å.

Table 2. Available Crystal Data for Monoclinic $P2_1/n$ Orpiment (Z = 4 As_2S_3 Formula Units) at Room Temperature

a (Å)	b (Å)	c (Å)	β (deg)	V/Z (Å^3)	ref
11.475(5)	9.577(4)	4.256(2)	90.68(8)	116.92	19
11.46	9.57	4.22	90.5	115.7	21
11.4223(4)	9.584(3)	4.258(2)	90.34(5)	116.53	22
11.40(1)	9.57(2)	4.307(1)	90.4(2)	117.47	23
11.432(4)	9.583(2)	4.255(1)	90.45(2)	116.54	this work[a]

[a] See also Table 4.

samples previously molten then recovered in the glassy state at room temperature.

Liquid density measurements were performed in the 750−1250 K range, and the subsequent specific volumes are shown in Figure 4.

4. Discussion

Table 1 shows that two incoherent sets of experimental values for the melting enthalpy of orpiment (either 77−78 or 117−122 J g^{-1}) at its temperature of fusion are found in the literature. In addition, $\Delta_{\text{fus}}H$ was estimated to be 94.83 J g^{-1} at 298 K,[16] and specific heat values for orpiment and As_2S_3 liquid were determined: C_p(s), J g^{-1} = 0.417 78 + (1.7142 × 10^{-4} × T, K)[13] or C_p(s), J g^{-1} = 0.429 40 + (1.4812 × 10^{-4} × T, K)[15] and C_p(l), J g^{-1} = 0.690 15 + (2.9892 × 10^{-5} × T, K)[13] or C_p(l), J g^{-1} = 0.722 92 + (6.8534 × 10^{-5} × T, K),[15] respectively. Incorporating these data into the Kirchhoff equation entails that the $\Delta_{\text{fus}}H$ value at 598 K should be within 158−172 J g^{-1} if the melting enthalpy at 298 K is used as a starting value.

Vapor pressure data for As_2S_3 have also been determined. In particular, curves P, Pa = 2.9607 × 10^{-16} × exp(0.071 972 × T, K)[24] and P, Pa = 0.128 43 × exp(0.014 015 × T, K)[25] for the solid−vapor and liquid−vapor equilibria, respectively, are found to cross at $P \approx 445$ Pa and $T \approx 581.5$ K, which corresponds to the approximate coordinates for the melting triple point of orpiment. Sublimation and ebullition enthalpies ($\Delta_{\text{sub}}H = 153$ and $\Delta_{\text{eb}}H = 84$ kJ mol^{-1}, respectively) calculated from these equations lead to $\Delta_{\text{fus}}H = 69$ kJ mol^{-1}, that is, 140 J g^{-1}, if the vapor phase is assumed to be made of molecular As_4S_6 units, although such a molecule was not observed through mass spectrometry.[26]

Table 3. Temperatures and Apparent Heats of Fusion ($\Delta_{\text{Fus}}H^*$) of Synthetic and Natural As_2S_3[a]

DSC analyzer	sample mass (mg)	T_{fus} (K) (onset)	$\Delta_{\text{fus}}H^*$ (J g^{-1})
Synthetic Sample			
A	9.83	602	128
A	9.13	601	123
A	2.58	599	122
B	20.63	599	122
B	14.05	601	137
B	13.81	599	124
B	11.94	602	134
C	13.812[b]	602	132
C	1.459[b]	598	121
C	1.368[b]	596	116
C	1.282[b]	602	119
C	1.133[b]	604	109
C	1.034[b]	598	105
C	0.914[b]	604	104
C	0.711[b]	597	93
C	0.492[b]	598	97
C	0.309[b]	602	58
C	0.277[b]	605	69
C	0.260[b]	601	52
Natural Sample P, from the Faculty of Pharmacy of Paris			
A	15.35	591	126
B	33.42_5	594	138
C	30.65	590	133
C	17.71	591	132
C	11.91	590	133
C	5.70	589	125
C	3.37	590	126.5
C	2.05	591	117
C	0.92	588	108
C	0.43	592	72.5
Natural Sample B, from the University of Barcelona			
A	11.77	597	126
A	7.10	596	134
B	7.20	593	118
C	6.25	595	137
C	4.57	597	123
C	0.835[b]	595	105.5
C	0.654[b]	597	103
C	0.255[b]		46

[a,b] Heating rate: 5 K min^{-1}. DSC analyzers: TA2000 (A) and TA-2920-MDSC (B) from TA-Instruments and DSC822^e(C) from Mettler-Toledo. Sample masses were weighed by means of microbalances sensitive to 0.01 mg or 0.001 mg (denoted by superscript b).

As far as the temperature of fusion of natural as well as synthetic orpiment is concerned, it can be seen in Table 1 that experimental T_{fus} values found in the literature scatter within 577−599 K. Cernosek et al.[3] reported a DSC melting curve in which the melting temperature (580 K) virtually hits the temperature for point b in Figure 3. However, these authors, as well as Voigt and Jacob,[1] mentioned onset temperatures (596 and 599 K, respectively) close to the temperature for point c in Figure 3. Thus, the discrepancy between the data in Table 1 and the data in Table 3 might be related to how the melting temperature is determined. Furthermore, data in Table 3 reveal that the mean value for T_{fus} of the synthetic sample (601(3) K) is greater than the mean values of the natural samples B (596(2) K) and P (591(3) K), and this might be related to a greater purity of the synthetic sample although no obvious difference in the composition of the natural samples was found through elemental analysis.

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(21) Morimoto, N. *Mineralog. J. (Jpn.)* **1954**, *1*, 160.
(22) Stojanovic, M. *Zapisnici Srpskog Geoloskog Drustva* **1982**, 51.
(23) Barrese, E.; Maras, A.; Plescia, P. *Neues Jahrb. Mineral.* **1994**, *4*, 167.
(24) Gospodinov, G. G.; Pashinkin, A. S. *Izv. Akad. Nauk SSSR, Neorg. Mater.* **1974**, *10*, 2074.
(25) Ustyukov, G. P.; Kudratsev, A. A.; Kuadze, B. M. *Izv. Akad. Nauk SSSR, Neorg. Mater.* **1968**, *4*, 1338.
(26) Faure, F. M.; Mitchell, M. J.; Bartlett, R. W. *High Temp. Sci.* **1973**, *5*, 128.

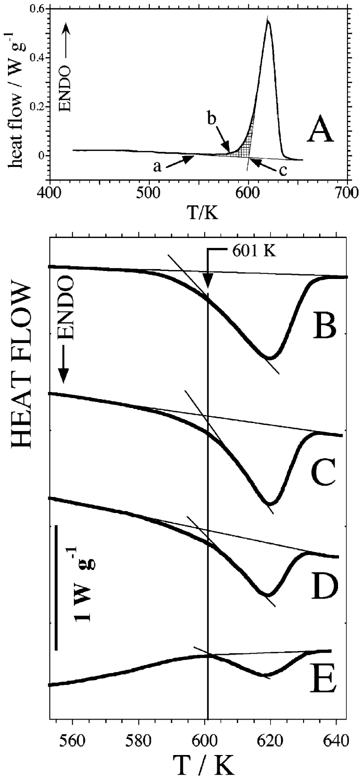

Figure 3. Synthetic orpiment. The DSC curve A, recorded at 5 K·min^{-1} using a TA-2920-MDSC analyzer, shows the (endothermic) melting peak and the sublimation-related premelting effect (hatched area) from *T*(a) to *T*(c), the onset temperature of the peak ($V/m = 2.135$ cm^3·g^{-1}). The DSC curves B–E were recorded at 5 K·min^{-1} using a Mettler DSC 822^e analyzer ($V/m = 2.2$ (B), 20.6 (C), 42.2 (D), and 97.0 (E) cm^3·g^{-1}). These curves are normalized to the same initial sample mass. It can be seen that the area of the apparent melting peak ($\Delta_{fus}H^*$) decreases as V/m increases.

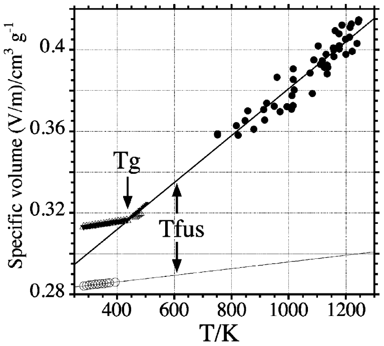

Figure 4. Specific volumes for orpiment (empty circles), vitreous As_2S_3 and metastable liquid (empty triangles, ref 33, and full triangles, ref 29), and stable liquid (full circles), as a function of the temperature. T_g and T_{fus} = temperatures of the glass transition and of the fusion, respectively.

Let us now remember that As_2S_3 sublimes and, as the temperature increases, the vapor pressure increases high enough so that thin initially flat covers of DSC pans (from Mettler) turn round-shaped after heating to 650 K. This was not observed when thick covers and pans (from TA Instruments) were used, thus indicating that these pans resist pressure better than the former do. Because the inner volume of any DSC pan cannot be completely filled with solid, a "dead" volume exists and becomes saturated with vapor when any DSC experiment is run. Even if the loss of condensed matter through partial sublimation before melting remains small and because any heat of sublimation is far greater than any heat of fusion, partial sublimation should be accompanied with an endothermic shift of the baseline part that precedes the melting peak in any DSC curve. Such a "premelting" endothermic effect can be seen (hatched area) between point a and point c of the DSC curve A in Figure 3. In addition, it is known that the temperature and thus the vapor pressure of the sample remain constant while the melting process occurs. This entails that the conditions under which any sample melts approximate the conditions of any triple point involving the vapor phase.

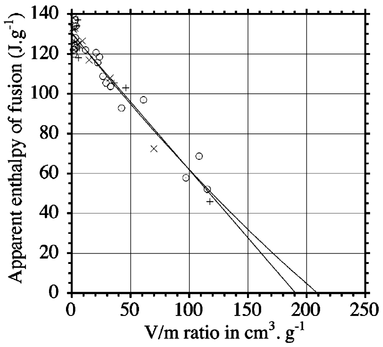

Figure 5. Apparent enthalpy of fusion ($\Delta_{fus}H^*$) for crystalline orpiment as a function of V/m (V = inner volume of the DSC pan, m = initial mass of sample). o = synthetic sample, + = natural sample B, and × = natural sample P. Curve fits (dotted lines). Linear: $\Delta_{fus}H^*$, J g^{-1}) = 130.02 − [0.682 86 × (V/m)], $r^2 = 0.940$. Polynomial: $\Delta_{fus}H^*$, J g^{-1} = 130.55 − [0.743 58 × (V/m)] + [0.000 575 36 × (V/m)]^2, $r^2 = 0.941$, V/m in cm^3 g^{-1}.

Now taking into account that the DSC runs were performed using pans with inner volumes of 30 μL and assuming that this volume remained almost constant over each run, the apparent heats of fusion, $\Delta_{fus}H^*$ in Table 3, can be drawn as a function of V/m (V = inner volume of the pan, m = initial mass of sample in the pan), as previously done to determine the heats of fusion of arsenic[27] and adamantane.[28] The graph in Figure 5 unambiguously shows that $\Delta_{fus}H^*$ depends almost linearly on V/m and that the value extrapolated to $V/m = 0$ is close to 131 J g^{-1}. As far as the premelting effect is concerned, it may be assumed that it should decrease with respect to the melting effect (see curves B–D in Figure 3) as the dead volume decreases because less matter has to sublime for the dead volume to be saturated with vapor. Hence, the real $\Delta_{fus}H$ value should be obtained by extrapolating $\Delta_{fus}H^*$ to $V/m = 0$. Indeed, $\Delta_{fus}H^*$ should be rigorously extrapolated to $V/m = v(l)$, the specific volume of the liquid-phase whose formation from the solid (s) at T_{fus} is accompanied with the positive volume change $v(l) - v(s)$. Nevertheless, $v(l)$ and $v(s)$ are very small against the specific volume $v(v)$ of the vapor phase at T_{fus} and can thus be neglected for extrapolating $\Delta_{fus}H$. Furthermore, it may be noticed that the specific volume $v(v)$ of the vapor phase at T_{fus} equals the V/m value for $\Delta_{fus}H^* = 0$. A $v(v)$ value of about 190–210 cm^3 g^{-1} is thus found, depending on how the curve fit is worked out. With these values, the vapor pressure at T_{fus} can be tentatively estimated using the ideal gas equation of state. It comes to $p \approx 5 \times 10^4$ Pa if the mass of the As_4S_6 unit is taken as the molar mass.

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(27) Rouland, J. C.; Céolin, R.; Souleau, C.; Khodadad, P. J. *Therm. Anal.* **1982**, *23*, 143.

(28) Espeau, P.; Céolin, R. *Thermochim. Acta* **2001**, *376*, 147.

Table 4. Monoclinic As_2S_3 (Orpiment): Lattice Parameters and Unit-Cell Volume as a Function of the Temperature ($Z = 4$ As_2S_3 Formula Units)

T (K)	a (Å)	b (Å)	c (Å)	β (deg)	V (Å^3)	V/Z (Å^3)
283.15	11.4136	9.5708	4.2530	90.4331	464.567	116.142
293.15	11.4132	9.5732	4.2544	90.4316	464.826	116.206
303.15	11.4133	9.5761	4.2560	90.4239	465.143	116.286
313.15	11.4129	9.5792	4.2569	90.4248	465.381	116.345
323.15	11.4139	9.5820	4.2585	90.4345	465.737	116.434
333.15	11.4132	9.5851	4.2595	90.4166	465.964	116.491
343.15	11.4139	9.5880	4.2607	90.4229	466.260	116.565
353.15	11.4131	9.5906	4.2611	90.4193	466.399	116.600
363.15	11.4133	9.5938	4.2627	90.4342	466.739	116.685
373.15	11.4132	9.5969	4.2638	90.4257	467.011	116.753
393.15	11.4142	9.6032	4.2652	90.4034	467.509	116.877

As far as the specific volume of the melt is concerned, new experimental results in the 750−1250 K range are shown in Figure 4 together with values from the literature for the glass and the undercooled melt in the 435−580 K range. Coherent data for the room-temperature values of the specific volume of the glass are found in the literature: 0.3131 (at 299 K),[29] 0.3138,[30] 0.3136 (at 297 K),[31] and 0.3115 cm^3 g^{-1} (at 296 K).[32] The specific volumes for the glass and the undercooled melt at $T < 600$ K were calculated using $\upsilon_T = \upsilon_0 \exp 3\alpha\Delta T$ and the linear thermal expansion coefficients for the glass ($\alpha(g) = 2.2 \times 10^{-5}$/K[33] or 23.33×10^{-5}/K[29] in the 298−435 K range) and the undercooled melt ($\alpha(l) = 9.6 \times 10^{-5}$/K[33] or 12.68×10^{-5}/K[29] in the 435−580 K range).

It can thus be seen that the values in the 435−580 K and 750−1250 K ranges agree with each other, despite some scattering in the high-temperature range. Such a scattering originates in the difficulty of locating the meniscus that separates the melt from the vapor. As the temperature increases, the liquid, which is red-brown at lower temperatures, turns to orange while the vapor darkens from yellow to orange, and the meniscus becomes less visible. From about 1150 K, the liquid and the vapor exhibit the same orange color, and the border between the two phases is still visible because the inner wall of the silica tube is wetted by the melt only. The specific volume values, in the literature as well as in the present work, for liquid As_2S_3 (Figure 4) were fitted to the equation $\upsilon(l)$, cm^3 g^{-1} = 0.265 84 + (11.504 × 10^{-5} × T, K) ($r^2 = 0.9794$). This corresponds to a volumic expansion coefficient of about 328 × 10^{-6} K^{-1}, which is near (358 ± 15) × 10^{-6} K^{-1} previously found in the 620−1000 K range.[34]

As far as the specific volume of synthetic orpiment is concerned, it is shown in Figure 4 that it depends almost linearly on the temperature in the 263−393 K range: $\upsilon(s)$, cm^3 g^{-1} = 0.279 66 + (1.6371 × 10^{-5} × T, K) ($r^2 = 0.997\,93$). Expansion of the lattice parameters in this range (Table 4) goes together with the layered structure as it mainly occurs along direction b, which is almost perpendicular to the As_2S_3 layers. Regarding the volume change of orpiment upon melting, it can be concluded that it is positive and depends almost linearly on temperature: $\Delta_{fus}\upsilon$, cm^3 g^{-1} = $\upsilon(l) - \upsilon(s) = -0.018\,29 + (9.8669 \times 10^{-5} \times T$, K).

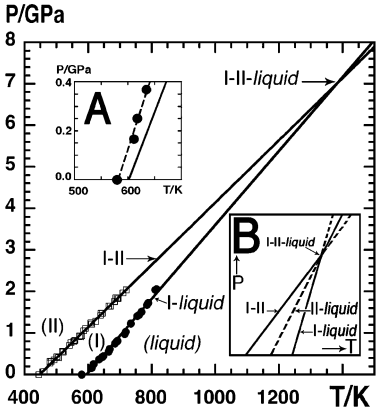

Figure 6. $p-T$ diagram of As_2S_3, according to refs 6 and 8. II = orpiment. Temperatures of transition I−II (empty squares) and form I melting (full circles) as a function of the pressure. Inset A: Experimental melting curve (dashed line) in the low P range compared with the calculated curve (thick line, this work). Inset B: Schematic representation of the two-phase equilibrium curves, according to the alternation rule that indicates how stable parts and metastable counterparts of the two-phase equilibrium curves do alternate around the I−II−liquid triple point (full lines = stable parts, dashed lines = metastable counterparts).

The glass transition for the synthetic glass was found to occur at $T_g \approx 477$ K (midpoint). This is in agreement with the 478 K value reported by other authors[13,30,31,33] who also studied synthetic samples. This is higher than the T_g value (453 K) previously found from vitrified natural samples[35] and also from glasses obtained after melting natural samples B (474 K) and P (471 K).

As far as the solid−solid transitions at ≈445 K[6] and/or at 540 K[7] are concerned, DSC experiments showed no trace for such events. In addition, the slopes dp/dT of the melting curves found by Devaud et al.[10] for orpiment (form II) and Kirkinskii et al.[6] for form I somewhat differ: about 60 MPa K^{-1} in the 577−700 K (0−2 GPa) range and about 89 MPa K^{-1} (mean value) in the 579−820 K (0−2 GPa) range, respectively.

Incorporating $\Delta_{fus}H(II) = 131$ J g^{-1}, $T_{fus}(II) = 601$ K, and $\Delta_{fus}\upsilon(II) = 0.041$ cm^3 g^{-1} into the Clapeyron equation gives the 53 MPa K^{-1} value for the slope dp/dT of the melting curve of orpiment in the As_2S_3 $p-T$ diagram, as an outcome of the present work.

Tonkov,[7] in a summary of Kirkinskii et al.'s work,[6] has reported that form II (orpiment) transforms at 443 K into form I that, itself, melts at 583 K. Tonkov also reported that these phase changes are accompanied with 2% (about 1% in the original paper[6]) and 10.9% volumic expansions, respectively. Assuming that $\Delta\upsilon(II\rightarrow I)$ is constant and taking $\upsilon(l) = 0.3329$ cm^3 g^{-1} at 583 K (as extrapolated from this work), it comes to $\upsilon(II) = \upsilon(l)/1.129 = 0.2949$ cm^3 g^{-1} at 583 K, close to the value (0.2892 cm^3 g^{-1} at 583 K) extrapolated from the present work. Now incorporating $\Delta_{fus}\upsilon(II) = 0.038\,27$ cm^3 g^{-1} at 601 K calculated from $\upsilon(l) = 1.129 \times \upsilon(II)$, according to Tonkov,[7] it comes to dp/dT

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(29) Haggerty, J. S. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, 1966; p 104.

(30) Tsuchihashi, S.; Kawamoto, Y. J. *Non-Cryst. Solids* **1975**, *17*, 369.

(31) Doupovec, J.; Thurzo, I.; Barancok, D.; Shilo, V. P. *Mater. Res. Bull.* **1977**, *12*, 119.

(32) Claytor, T. N.; Sladek, R. J. *Phys. Rev. B* **1978**, *18*, 5842.

(33) Málek, J. *Thermochim. Acta* **1998**, *311*, 183.

(34) Ananichev, V. A.; Baidakov, L. A.; Balbmakov, M. D.; Blinov, L. N. *Fizika I Himia Stekla* **1982**, *8*, 637.

(35) Frumar, M.; Firth, A. P.; Owen, A. E. *J. Non-Cryst. Solids* **1995**, *192−193*, 447.

= 57 MPa K^{-1} at 601 K for the melting curve of orpiment. It is to be noticed that this value is near the value (62.5 MPa K^{-1}) reported[6,7] for the initial slope of the melting curve of form I. This entails that the form II melting curve inferred from the present work is close and almost parallel to the experimental melting curve of form I[6,8] in the low-pressure range of the $p-T$ diagram (see inset A in Figure 6).

In addition, according to the experimental $p-T$ diagram[6,7] (see Figure 6), the I−II transition curve and the form I melting curve should cross at the I−II−liquid triple point, located at high pressure and high temperature. According to the alternation rule (see inset B Figure 6), this entails that (i) the II−liquid curve should be stable at pressures and temperatures greater than those of the I−II−liquid triple point, (ii) the slope dp/dT of the form II melting curve should be smaller than that of the form I melting curve and greater than that of the I−II transition curve (see inset B, Figure 6), and (iii) the metastable counterpart of the form II melting curve should intercept the abscissa (at $P \approx 0$) at a temperature smaller than that of the form I melting curve. It is worth noting that such inferences conflict with all the experimental results regarding the melting temperature of form II (orpiment) unless the experimental melting curve related to form I is the melting curve of orpiment.

Thus the existence of another enantiotropically related As_2S_3 polymorph remains elusive.

5. Concluding Remarks

This study shows that inconsistencies in the values of the melting enthalpy of synthetic orpiment might be explained as an effect of the vapor pressure that is no longer negligible at the temperature at which orpiment melts. In other words, this work exemplifies how neglecting non-negligible vapor pressures leads to conflicting data on melting enthalpies, and it shows how the ratio V/m can act as a remedy for this situation, if the melting point is thought up as a triple point involving the vapor phase.

Regarding the phase transition from dark yellow orpiment into a dark red form, reported by Kirkinskii et al.,[6] it is to be noticed that these authors used a natural sample from a Georgian deposit whose elemental analysis showed about 1−2% antimony as the main impurity. Thus, it might be tentatively suggested that this phase transition is related to (or induced by) such an impurity.

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