Pis'ma v ZhETF, vol. 98, iss. 9, pp. 608 – 612

High-pressure polymorphism of As_2S_3 and new AsS_2 modification with layered structure

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Submitted 11 September 2013

At normal pressure, the As_2S_3 compound is the most stable equilibrium modification with unique layered structure. The possibility of high-pressure polymorphism of this substance remains questionable. Our research showed that the As_2S_3 substance was metastable under pressures $P > 6$ GPa decomposing into two high-pressure phases: $As_2S_3 \rightarrow AsS_2 + AsS$. New AsS_2 phase can be conserved in the single crystalline form in metastable state at room pressure up to its melting temperature (470 K). This modification has the layered structure with $P12_11$ monoclinic symmetry group; the unit-cell values are $a = 7.916(2)$ Å, $b = 9.937(2)$ Å, $c = 7.118(1)$ Å, $\beta = 106.41°$ ($Z = 8$, density $3.44\,\mathrm{g/cm^3}$). Along with the recently studied AsS high-pressure modification, the new AsS_2 phase suggests that high pressure polymorphism is a very powerful tool to create new layered-structure phases with "wrong" stoichiometry.

DOI: 10.7868/S0370274X13210054

1. The study of the As–S system under both high and normal pressure is of a large applied importance from the standpoint of developing new materials with a desired set of properties, due to a wide variety of compounds with different compositions existing within this system. Among arsenic sulfides, As_2S_3 (mineral orpiment) is unique. The structure of this mineral, unlike (pseudo-)molecular structures of the majority of compounds of S atoms with As atoms, is a layered quasi-two-dimensional structure [1, 2]. This structure mainly controls optical properties of compounds and materials based on such kind of packing [3]. In addition, As_2S_3 from structural point of view is considered as a prototype of glasses and amorphous phases of As_2S_3 and As_2Se_3, which are very important materials extensively used in optics and electronics. It is supposed that parts of quasi-two-dimensional layers are present in corresponding glasses and amorphous phases. Moreover, there is an analogy between the topologies of bonds in crystalline As_2S_3 and the corresponding glass that serves as the basis for the famous "continuous network" model of amorphous materials.

Orpiment As_2S_3, as distinct from the majority of the other well-known layered compounds such as PbI_2, TaS_2, GaSe, does not exhibit any polytypism (polymorphism based on the repacking of layers). It is believed that this property is due to a structural complexity (low symmetry, large unit cell) of an individual layer in orpiment (Fig. 1). Horizontal layers are perpendicular to the figure plane and are corrugated in the shape of trapezium. There are no strong covalent bonds between the layers. The packing in an As_2S_3 crystal can be presented in a simplified form as fitting of "thick" and "thin" sites of neighboring layers. Such a dense packing of layers can be attained in the only way, as distinct from numerous, close in energy, packages of the highly symmetric structures of PbI_2, TaS_2, GaSe.

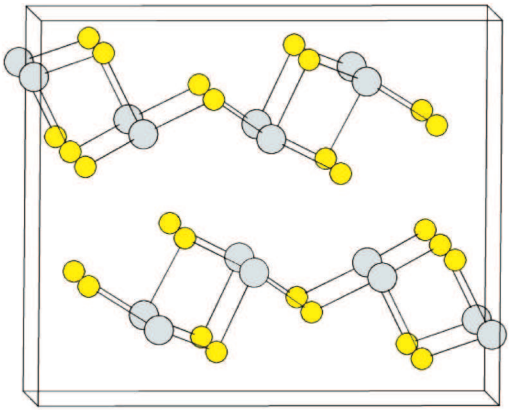

Fig. 1. (Colored online) The layered structure of As_2S_3 orpiment in volume of unit cell. Grey circles are As atoms, yellow – S atoms

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The remarkable packing of layers in orpiment is responsible for its high stability under pressure. The compression to 10 GPa does not lead to any phase transformations at room temperature. However, the interaction between layers increases under pressure noticeably and the optical gap decreases from 2.7 to 1.6 eV at 10 GPa [4]. Therefore, a widely accepted opinion has formed that a phase transition in As_2S_3 is possible only under super high pressures ($\gg 10$ GPa), when the reconstruction begins inside each layer leading to the increasing of coordination numbers of the atoms. In particular, it was predicted in [5] that the phase transition in As_2S_3 will take place at 35–40 GPa. Evidently, the transition of that kind will be accompanied by metallization. The metallization at the structural transformations under high pressures in glassy As_2S_3 has been more extensively studied (see [6] and refs therein). The possible polymorphism of crystalline As_2S_3 modification has not been explored at pressures higher than 10 GPa. At the same time, it could be supposed that a phase transition to a denser As_2S_3 modification is also possible under elevated temperatures and moderate pressures (< 10 GPa). The simultaneous action of high pressure and temperatures on As_2S_3 was previously investigated in [7–13]. In [11] it has been found that crystalline orpiment is the most stable phase under pressures at least up to 3 GPa. In [7–10] at higher pressures (6–7 GPa) a high-pressure phase (or even two phases) was obtained. The new modification(s) was red in color and its structure was not determined. Moreover, recently it has been suggested that the new phase could have the composition corresponding to As_2S_5 compound [12]. In any case, a hypothetic high-pressure phase of As_2S_3 remained questionable (in particular, it was suggested that reported in [7–10] phases actually represented multicomponent arsenic and sulfur compounds with the elements of a high pressure cell [14]).

In situ X-ray diffraction investigations of the As_2S_3 phase diagram (see also [13, 15]) detected an irreversible structural transformation under pressure above 6 GPa and temperature above 800 K (Fig. 2). The high-pressure phases are metastable at normal conditions. This result stimulated our attempts to grow large crystals of new high-pressure phase and to determine its structure.

2. The runs were performed using "Conak" type high-pressure chamber with an automatically controlled load and program-controlled power supply to the graphite heater. The temperature has been measured by a set of thermocouples; the pressure has been measured using manganin gauge. The As_2S_3 specimen (99.99% purity) was pressed into a container from

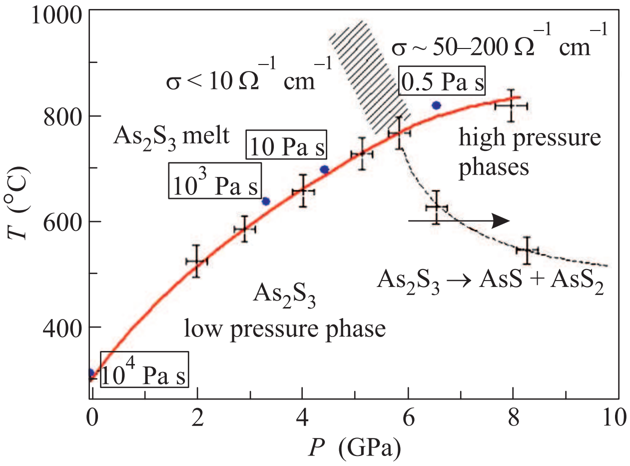

Fig. 2. (Colored online) Transitional phase diagram of As_2S_3

hexagonal boron nitride with the sizes: $h = 8$ mm, $\varnothing_{\rm out} = 6$ mm, and $\varnothing_{\rm in} = 3$ mm ($h_{\rm sample} = 3$ mm). In the solid state there was very high degree of hydrostaticity, whereas during crystal growth from melt there were pure hydrostatic conditions. The initial and final products, which were obtained under high pressure and temperature, were analyzed using of a DRON-3M diffractometer ($Cu_{k\alpha}$-radiation), single crystal Laue and Burger cameras, a JEOL scanning microscope and an Xcalibur single crystal diffractometer (Mo-radiation, graphite monochromator). The solution and refinement of the structure were performed in accordance with the JANA 2006 program [16]. Chemical compositions of the specimens were analyzed using a JED-23000 F micro analyzer of a JSM-6700 F (JEOL) scanning electron microscope.

3. The area of growth ($p = (5.5{-}6.0)$ GPa and $T = (1100{-}850)$ K) was chosen in accordance with $P{-}T$-diagram of As_2S_3 [13]. The As_2S_3 sample was cooled with an average rate of 1 K/min within this temperature interval at fixed pressure. After the container was opened, the specimen was a well-crystallized mass of carmine-red color with the grain from 5 to 30 μm mixed with thin black matrix. Central zone included fine-shaped crystals up to 0.5 mm in size with a perfect oblique cleavage, as well as crystals of an elongated habit $30\times30\times200\,\mu m^3$ in size (Fig. 3). The latter were selected for a complete structural analysis by which it was established that the chemical composition of these crystals corresponded to the AsS_2 formula. This composition has been confirmed by the chemical analysis of the single crystals. The new AsS_2 structure was solved by the charge flipping method [16] in $P12_11$ monoclinic symmetry group. The unit cell values are $a = 7.916(2)$ Å,

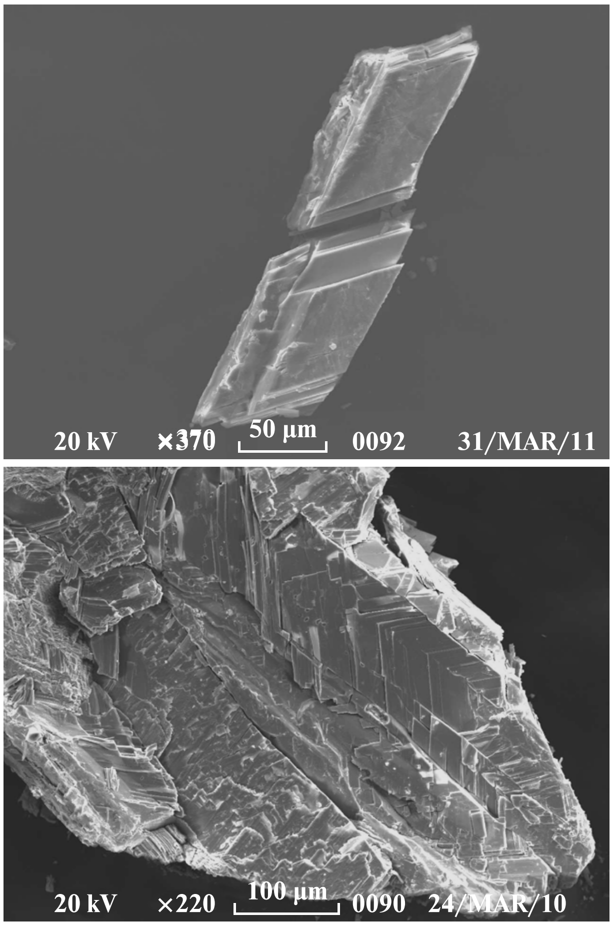

Fig. 3. Single crystals of AsS_2 grown in As_2S_3 pristine composition

$b = 9.937(2)$ Å, $c = 7.118(1)$ Å, $\beta = 106.41°$. The black tiny crystals correspond to the recently discovered AsS high pressure phase [17].

The structure of the new high-pressure AsS_2 phase is presented in Fig. 4 along with the previously studied layered structure of the high-pressure AsS phase [17] in the projection on the system of layers (Figs. 4a and c) and on the plane of a layer (Figs. 4b and d). Thus in our case we were able to define unambiguously the atomic structure of high-pressure phase. The atomic positions are presented in the Table.

The formation of the new AsS_2 compound makes it possible to conclude that As_2S_3 compound does not correspond to the minimum of Gibbs free energy at high pressure–high temperature region and undergoes the chemical decomposition at $P > 5.5$ GPa and $T > 800$ K in accordance with following reaction: $As_2S_3 \rightarrow AsS_2 + AsS$. To confirm this fact we performed series of experiments on the slow cooling of the melt with the AsS_2 chemical composition (we used pristine mixture As_2S_3 and S) under high pressure 6 GPa. The X-ray diffraction patterns of the red crystals obtained by quenching from liquids of As_2S_3 and AsS_2 composition both contained the identical lines of AsS_2 phase. According to the results of this analysis, the composition of AsS_2 single crystals grown from the As_2S_3 melt is As – $66.5 \pm 0.1\%$, S – $33.5 \pm 0.1\%$, and the composition of AsS_2 single crystals grown from the AsS_2 melt is As – $65.2 \pm 1.4\%$, S – $34.8 \pm 1.4\%$. Investigation of the chemical composition of the massive part of the specimen obtained from the As_2S_3 melt revealed the existence of regions corresponding to the AsS composition. We did temperature-dependent structural study of the new phase at normal pressure. Under heating at room pressure new AsS_2 phase melts to undercooled liquid at 470 K. One should mention that pressure-induced decomposition occurs in large number of minerals, for example, some silicates, aluminates, zirconium tungstate, zirconium vanadate, scandium molybdate etc. However, this phenomenon has been observed for the first time for the simple binary chalcogenides.

Atomic positions in the AsS_2 structure

Atom	x/a	y/b	z/c
As1	0.9706(5)	0.038496	0.4108(5)
As2	0.4358(4)	0.0526(6)	0.2616(5)
As3	0.6543(4)	0.8225(5)	0.1065(5)
As4	0.8772(5)	0.3219(6)	0.0282(5)
S1	0.6080(9)	0.0436(10)	0.0489(10)
S2	0.1861(9)	0.5302(9)	0.3561(11)
S3	0.7163(9)	0.3240(10)	0.2774(10)
S4	0.9389(9)	0.8256(9)	0.2970(10)
S5	0.1634(12)	0.0417(13)	0.0499(14)
S6	0.4717(9)	0.8331(10)	0.3304(10)
S7	0.1628(10)	0.3501(9)	0.2346(11)
S8	0.7508(13)	0.5232(12)	0.4124(14)

Thus, the previous interpretations of the red phase prepared from As_2S_3 substance at high pressure–high temperature conditions as new As_2S_3 modification [7–10] or As_2S_5 compound [12] were erroneous. The density of new AsS_2 compound at normal condition is $3.44\,g \cdot cm^{-3}$; it is slightly less than the density of pristine orpiment As_2S_3 ($3.49\,g \cdot cm^{-3}$). However, due to larger density of AsS high pressure phase – $4.07\,g \cdot cm^{-3}$ [17] the decomposition reaction $As_2S_3 \rightarrow AsS_2 + AsS$ has negative volume effect (8%) and hence high pressure promotes this process.

AsS_2 modification gives second example of layered structure with “wrong” stoichiometry in As–S system. The layers in the AsS_2 structure are not only weakly bound to each other but they consist of separate weakly

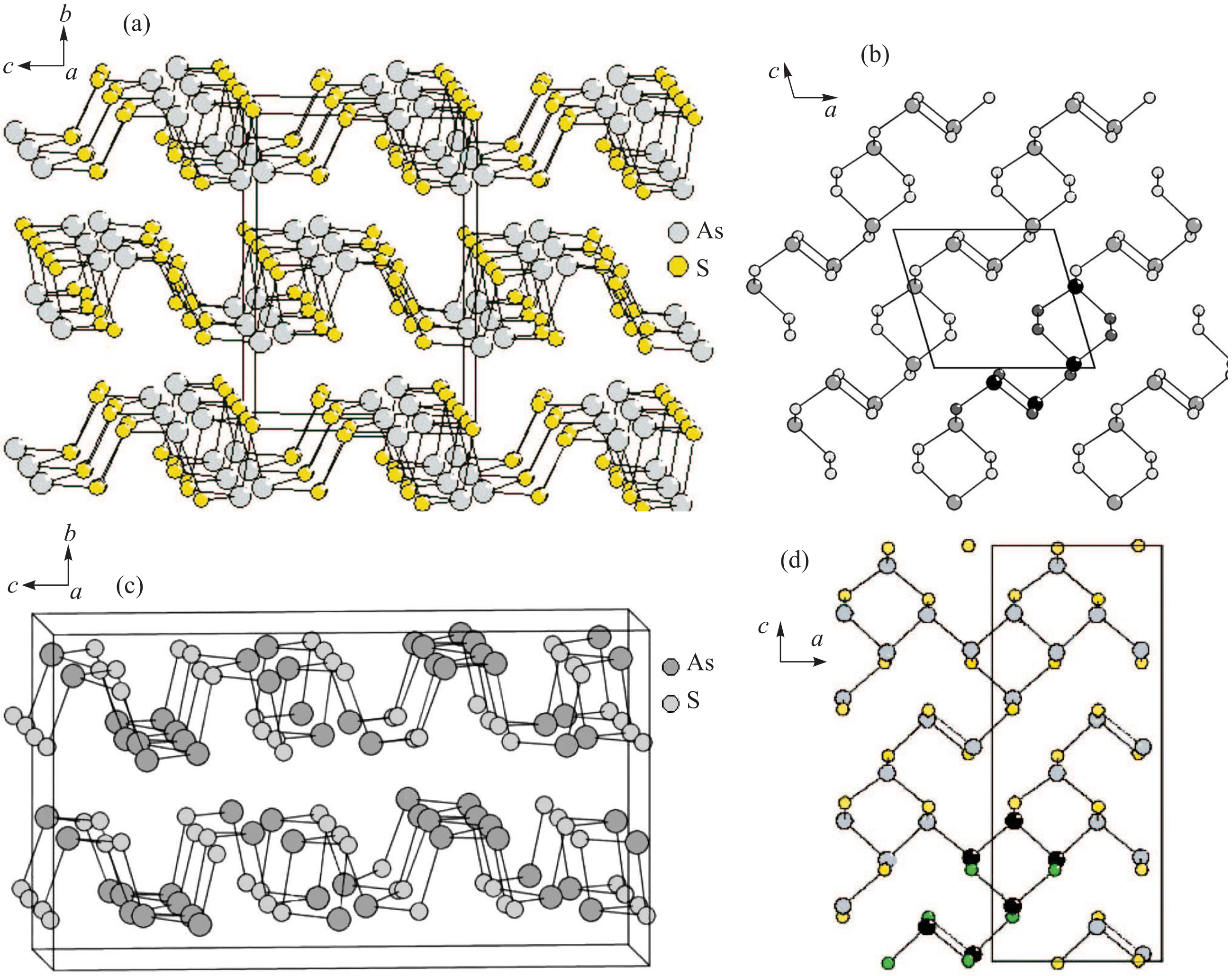

Fig. 4. (Colored online) The systems of layers and the plane of individual layer in the structure of high-pressure phases of AsS_2 (a, b) and AsS (c, d). Grey circle are As atoms, yellow – S atoms. Similar fragments of two structures in layer are stood out by color

bound zigzag columns which are extended along the diagonal in the layer plane (Figs. 4a and b). For comparison, it could be noticed that in the previously studied AsS high-pressure phase, the layers are also weakly bound and also contain diagonal columns which are united by the chains of As atoms extended horizontally. The columns and the chains form together a two-dimensional network (Figs. 4c and d), supposedly ensuring a large strength of this material in comparison with AsS_2.

In addition, two structures differ in the atomic coordination. In the AsS structure, one half of As atoms have two As atoms and one S atom as its neighbors, and the second half of As atoms are coordinated by three S atoms, whereas all S atoms have two As atoms as its neighbors. All As atoms in the AsS_2 structure are bounded only to three S atoms and one half of S atoms are coordinated with two As atoms, and the other half of S atoms – with one S atom and one As atom.

One should mention that the "wrong stoichiometry" is well-known for some layered compounds, for example MgB_2, however it is very rare in chalcogenide compounds due to the strong covalent bonding.

X-ray diffraction patterns of the AsS_2 single crystals, which are grown from its own melt, indicate that the quality of the crystals is substantially worse, what may be caused by a high viscosity of the melt. The viscosities along with electric resistances and structures of AsS and As_2S_3 melts under pressure are studied in [13, 15]. The structural investigations indicate that the number of As–As nearest neighbors increases in these melts at such pressures. One can suggest that liquid As_2S_3 is "inhomogeneous" on a scale of 2 nearest coordination spheres: the melt represents a network structure enriched in sulfur atoms, with the AsS_2 composition, including regions enriched in arsenic (with As–As pairs). In this case, the decomposition of the liquid As_2S_3 compound during cooling is quite explainable. The AsS_2 compound, which does not exist at low pressures, has a network structure of high-viscosity melt even at very high pressures. This fact is confirmed in our experiments on rapid quenching from the AsS_2 melt. A glass is formed at a rapid cooling ($10\,K \cdot s^{-1}$) of AsS_2 melt up to pressures of 8 GPa and crystals can be grown under high pressure at slow cooling ($1\,K \cdot min^{-1}$) only.

Summing up, one can conclude that As_2S_3 compound at high pressures and high temperatures does not correspond to the most stable phase at this composition and decomposes into the mixture of two high pressure modifications – AsS_2 and AsS. AsS_2 phase gives the example of layered structure with "wrong" stoichiometry. The cost for the formation of a layered covalent structure at a non-stoichiometric composition is the presence of covalent bonds in the structure between the same type of atoms (S–S). Thus the high-pressure behavior of As_2S_3 substance demonstrates new interesting kind of "polymorphism" resulting in the formation of new and unique crystalline structures.

The authors wish to thank S.M. Stishov and A.G. Lyapin for valuable discussions. This work has been supported by the Program of the Presidium of RAS P-02 and RFBR (11-02-00303).

1. D. J. E. Mullen and W. Nowacki, Zeitschrift fur Kristallographie **136**, 48 (1972).
2. Y. Shimoi and H. Fukutome, J. Phys. Soc. Jpn. **59**, 1264 (1990).
3. R. Zallen, R. E. Drews, R. L. Emerald, and M. L. Skade, Phys. Rev. Lett. **26**, 1564 (1971).
4. R. Zallen, High Pressure Research **24**(1), 117 (2004).
5. D. Gerlich, E. Litov, and O. L. Andersen, Phys. Rev. B **20**, 2529 (1979).
6. V. V. Struzhkin, A. F. Goncharov, R. Caracas et al., Phys. Rev. B **77**, 165133 (2008).
7. N. V. Timofeeva, G. Z. Vinogradova, E. M. Feklichev et al., Dokl. AN USSR **190**, 902 (1970).
8. N. V. Timofeeva, G. Z. Vinogradova, E. M. Feklichev et al., Modern Problems of Physical Chemistry (MSU) **6**, 234 (1972).
9. V. A. Kirkinskii, A. P. Ryaposov, and V. G. V. Yakushev, Izv. Akad. Nauk USSR, Neorg. Mater. **3**, 1931 (1967).
10. V. A. Kirkinskii, A. P. Ryaposov, and V. N. Korolik, *Experimental methods in mineralogy*, Novosibirsk, 1974.
11. G. Devand, M. J. Aziz, and D. Turnbull, J. Non. Cryst. Solids **109**(1), 121 (1989).
12. S. Pfeiffer, *Ph. D. Thesis*, Max-Planck-Institute fur Festkorperforschung, Stuttgart, 2009.
13. V. V. Brazhkin, Y. Katayama, M. V. Kondrin et al., Phys. Rev. B **82**, 140202 (2010).
14. P. Espean, J. L. I. Tamarit, M. Barrio et al., Chem. Mater **18**, 3821 (2006).
15. V. V. Brazhkin, Y. Katayama, M. V. Kondrin et al., Phys. Rev. Lett. **100**, 145701 (2008).
16. V. Petrichek, M. Duchek, and L. Platinus, *Structure Determination Software Programs, JANA 2006*, Institute of Physics, Praha, 2006.
17. V. V. Brazhkin, N. B. Bolotina, T. I. Dyuzheva et al., Cryst. Eng. Comm. **13**, 2599 (2011).