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PHASE EQUILIBRIUM IN THE BINARY SYSTEMS $A^{IV}B^{VI}$

Part. I. The systems Silicon –Chalcogen

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The phase structure and phase transition properties are reviewed in the binary systems based on silicon and chalcogen (sulphur, selenium and tellurium).

In order to control the synthesis of the individual chemical compounds or materials a leading role is played by the data that are encoded in the corresponding phase diagrams. Thus, by enriching the experimental data, the phase diagrams allow to consider the fundamental laws that govern the synthesis process. With the help of phase diagrams, it is possible to show clearly the true correlations between the physical-chemical parameters that determine the state of the system, i.e. the character of the interaction of the same components in various conditions. The phase diagrams are useful for every day work of researchers that develop new technologies and make new materials. During the rational design of the materials it is necessary to consider two features: thermodynamics, that includes basically the phase equilibrium at high temperature and pressure and answers to the questions of phase stability and crystallo-chemistry of the materials from which the final compound is obtained. For material producers are of interest not only the data on new phases, but also any other information, which can be obtained from the T-x-diagrams: the structure of liquidus, the coordinate of the non-variant points on liquidus and subsolidus domain, solubility of the components in the solid state, mode of formation and polymorphism of synthesized phases and others. Only knowing all these factors, it will be possible to choose correctly the composition of the material and to conduct correctly the melting processes of the initial materials, the synthesis of the materials and crystal growth. Of great importance for the control of the crystal growth with a given chemical composition is the knowledge of the phase microdiagrams, because even not significant deviations from stoichiometry can induce essential changes in the electronic properties. Thus, in the majority of the semiconducting $A^{IV}B^{VI}$ compounds, the type of conductivity and the concentration of the charge carriers can be controlled without the introduction of the doping elements, only by changing the ratio of the elements A and B in the determined limits. In order to control the modifications of the properties of these compounds it is important to know the limits to which the composition is modified for different temperatures. These limits are defined by the position of the boundaries of the compound homogeneity in the corresponding binary systems.

In the majority of the systems $A^{IV}B^{VI}$ the homogeneity domains are partially or completely shifted relative to the stoichiometric composition towards an excess of one of the components.

1.1 System Si - S

Today, the information on the stable phases in the system Si-S and Si-Se is limited. The lack of the completely investigated phase diagrams lead us to operate only with the results of research of the physical properties of their components and interactions with the components of the materials for high temperatures. A supplementary difficulty is given by the necessity to carry out all the measurements in the complete absence of air and of humidity. T-x-phase diagram for the binary system Si-S is poorly studied. According to [16-22] in this system are formed two chemical compounds: silicon monosulphide (SiS) and silicon disulphide (Si-Se). Fig. 1.1 shows the

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hypothetical phase diagram that summarize the known data on silicon sulfide [16]. The sulphurisation of Si gives rise to SiS_2, that exhibits the melting point 1363 K and the boiling point situated in the range 1373÷1473 K [14]. Silicon disulphide is obtained during the interaction of SiO_2 with Al_2S_3 at 1473 K ÷ 1573 K in a fluence of dry nitrogen [15]. SiS is formed during the interaction of SiS_2 with Si in vacuum at 1123 K [20]. Both chemical compounds decompose easily in water, especially in water vapors with the formation of SiO_2 and H_2S. By hydrolysis is released meta-silicon acid. Hydrolisis is accelerated in the presence of alkalis. SiS_2 is oxidized by air oxygen only during heating [15].

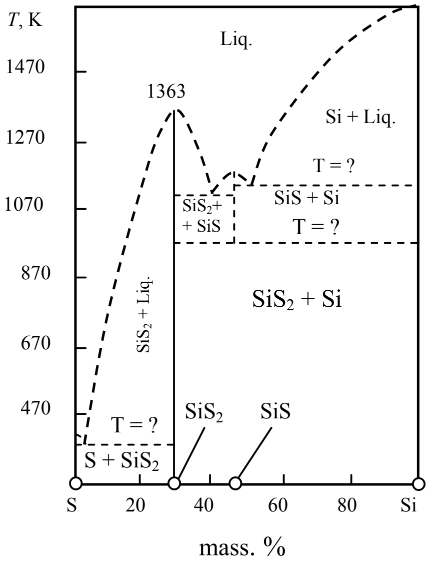

Fig. 1.1. The hypothetical phase diagram of the system Si-S [16].

The measurement of the equilibrium vapor pressure of the reaction:

$$\tfrac{1}{2}\,SiS_2 + \tfrac{1}{2}\,Si \rightarrow SiS \qquad (1.1)$$

and of the SiS_2 vapor by the effusion method of Knudsen, has shown that SiS_2 vapor pressure can be neglected if compared to the SiS vapor pressure [17]. The sublimation temperature of SiS is 1213 K [14]. Sublimation enthalpy of SiS_2 at 1000 K is equal to 258.476 kJ/mol. The temperature dependencies of the saturated vapor pressure are expressed by the equations:

for SiS: $\lg p$ (atm) = $-47200/4.573\,T + 31.6/4.573$ (894÷1076 K)
for SiS_2: $\lg p$ (atm)= $-61736/4.573$ T + $37.48/4.573$ (950÷1200 K).

The synthesis of the high pressure phases of SiS_2 was performed by the authors of [23]. For getting SiS_2 the mixture of Si and S (in atomic ratios 1:1, 2:3, 1:2 and 1:2.2) has been pressed and heated at 973 K under the pressure of 5 GPa. The SiS_2 thus obtained crystallizes in the tetragonal system, and in air at 870 K transforms in Si_2OS_3. Further heating in pure oxygen at 1273 K leads to the formation of SiO_2. In nitrogen, the high pressure phase SiS_2 is stable up to 1098 K. By heating at 1273 K under 4.5 GPa pressure during five minutes, one gets grey acicular crystals from the mixture Si and S with atomic ratio 1:2. By heating at 1673 K and 4.4 GPa during 5 minutes, yellow-brown crystals are formed. By heating at 973 K and 4.5 GPa during 5 minutes, are formed glassy products [23] for atomic Si and S ratios: 1:1, 2:3, 1:2 and 1:2.2.

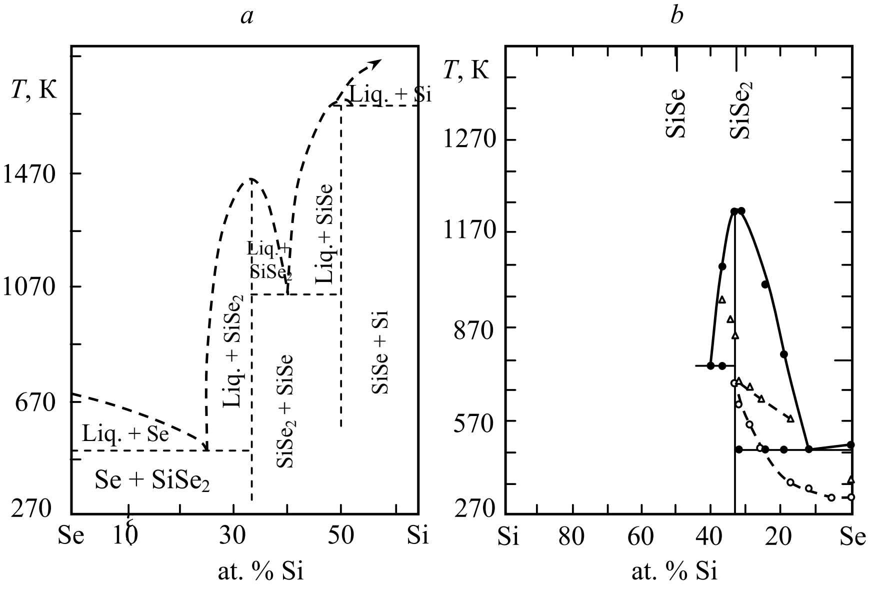

Fig. 1.2. a. The hypothetical phase diagram of the system Si-Se [24]
b. part of the phase diagram of the system Si-Se (after [25]).

1.2 System Si-Se

The T-x phase diagram of the system Si-Se was not studied systematically. The hypothetical phase diagram proposed in [24], is shown in Fig. 1.2 a. The experimental phase equilibrium diagram for the domain rich in selenium is given in Fig. 1.2 b [25]. In the system exist two chemical compounds: SiSe and $SiSe_2$ [21, 22, 24-27]. $SiSe_2$ is obtained by the direct melting of the elementary components in stoichiometric proportions [22, 27]. The study of the reaction between Se and Si in vacuum, carried out by ATD and X-ray diffraction methods, has shown that the endothermal reaction starts at 673 K, but for this temperature the reaction is slow and for completing the reaction a long heating time at 843 K is needed. The product of reaction is $SiSe_2$. The sublimation of $SiSe_2$ in air starts at 943 K. $SiSe_2$ melts congruently at 1243 ± 5 K [27]. Crystalline and glassy $SiSe_2$ hydrolize easily in humid air with the formation of SiO_2, H_2Se and red selenium. The density of the $SiSe_2$ is 3.6 g/cm^3 [28].

The compound SiSe melts incongruently, mainly following the reaction [24]:

$$2\ SiSe \rightarrow SiSe_2 + Si \qquad (1.2)$$

SiSe can be obtained by the interaction of SiO_2 with MgSe at 1523 K or by the interaction of $SiSe_2$ and Si at 1073 K, or by direct melting of Si and Se taken in stoichiometric proportions at 1023 K [18, 27]. The compound SiSe decomposes in water, acids and alkalis. There are not data to support the existence in the system Si-Se of an other compound: Si_2Se_3. All the information points to the fact that this composition corresponds to the eutectic point. The same situation occurs in the system Si-S.

Because there is not a reason to suppose the existence, between the compositions SiSe and $SiSe_2$, of stable binary chemical compounds, on the diagram one looks for a simple eutectic. Its temperature and composition are not known, but in [24] it is supposed that the eutectic is situated at $T<493$ K, and the content of silicon is under 30 at. % (Fig. 1.2).

1.3 System Si-Te

The system Si-Te has been investigated satisfactorily by DTA, XRD and tensiometry in the papers [29-31]. The T-x projection of the phase diagram of the system is shown in Fig. 1.3. Judging after the disposal of the lines on the T-x diagrams, the data reported by other authors [29, 30] are close to the representation in Fig. 1.3. There was established that in the system Si-Te is formed only one compound, Si_2Te_3, that melts incongruently at 1159 K [31], 1165 K [29] and 1168 K [30]. Only in the paper [129] it is shown that the compound Si_2Te_3 melts congruently at 1162 K. Red platelets crystals are easily obtained by static sublimation method [29,32].

In spite of the strong stability, if compared to the known compounds in the systems Si-S and Si-Se, the Si_2Te_3 crystals slowly hydrolyze. During the transfer of the crystals from vacuum to air, after some time the crystal surfaces cover with a film of tellurium, which protects the crystal from further decomposition. The surface reaction is described [32] by the equation:

$$Si_2Te_3 + 4\,H_2O \rightarrow 2\,SiO_2 + 2\,H_2\uparrow + Te + 2\,H_2Te\uparrow \tag{1.3}$$

The presence of SiO_2 and Te on the surface was proved by chemical analysis. H_2Te can be easily identified due to its characteristic smell. In the literature are indicated the polymorphous transformation Si_2Te_3 at 673 K [29, 130]. In the paper [31] are reported not very large, but significant effects at 683 K for the equilibrium alloys in the range 20÷60 at.% Te. An experiment was carried out to quench the high temperature modification β-Si_2Te_3 [31]. The samples were rapidly cooled in a mixture of water with ice started from 873 or 963 K (the samples were maintained at these temperatures for 24h) and the diffraction patterns were recorded immediately after quenching. XRD has evidenced the presence only of the lines of the low temperature modification α-Si_2Te_3.

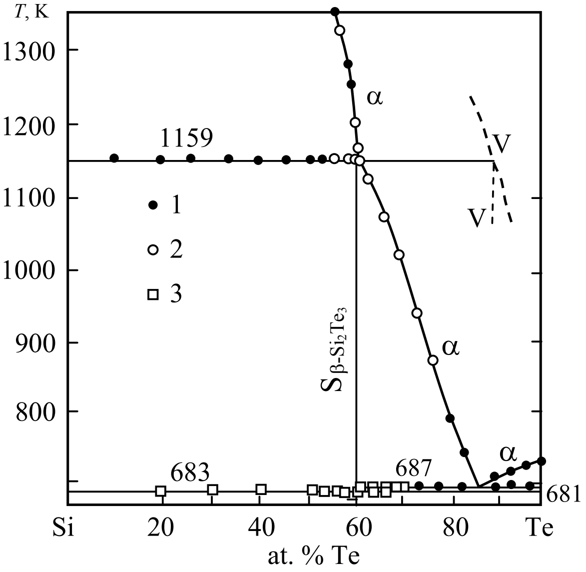

Fig. 1.3. Phase diagram of the system Si-Te [31]: 1 – data from the heating curves DTA; 2 – DTA data for simultaneous determination of the vapor pressure; 3 - DSC data.

The phase Si_2Te_3 sublimates incongruently and this fact results from the mass-spectrometry [33] and tensiometry [31] data:

$$Si_2Te_3\ (\text{cryst.}) \rightarrow (2-x)\ Si\ (\text{cryst.}) + [(3-x)/2]\ Te_2\ (\text{vapour}) + x\ SiTe\ (\text{vapor})$$

According to mass-spectrometry data, the fundamental particles in the vapor phase above crystalline Si_2Te_3 are the molecules Te_2 and SiTe. The $SiTe_2$ molecules are present only in a not significant amount.

The conclusions regarding the boundaries of the homogeneity domain of the Si_2Te_3 are contradictory. During the study of the section p_{Te2}-T of the system it was established [34] that the homogeneity domain does not overcome the limits of compositions 59.45 and 60.50 at.% Te. The authors of the paper [130] believe that the homogeneity domain is situated in the range 60 ÷ 66.6 at.

% Te, i.e. from Si_2Te_3 to $SiTe_2$. A definite answer to this question has been given in [31]. The authors used three independent methods: XRD, microstructural analysis and tensiometry. The largest domain (from 59.6 to 60.25 at.%) was obtained by XRD. Nevertheless, as reported by the authors of [31], the observed boundaries are only orientative because the XRD method is sensitive in the limit of 0.5 weight % relative to the second phase. More precise data are given by tensiometry: from 59.85 ± 0.06 at.% to 60.14 ± 0.04 at. % (at 1023 K). The tensiometric determination of the boundaries has several advantages. Firstly, the precision is very high (for Si_2Te_3 around 0.05 at.%). Secondly, the experiment is carried out at the temperature, where the homogeneity domain is determined, and for vapor pressure that corresponds to the studied equilibrium [31].

The eutectic between Te and Si_2Te_3 exhibits relatively low melting temperature (682 K) and corresponds to an approximate composition 17÷18 at.% Si [29]. The presence of the eutectic in the system Si-Te, with the parameters: 82.5 at.% Te and melting temperature 679 K, is supported in [30]. In this composition domain the viscosity of the melt is enough significant, and, therefore, in these conditions it is possible to harden the melt with the formation of glass. The thermal effects in the vicinity of 683 K are related to the phase transformation in the solid state toward Si_2Te_3.

In spite of the fact that on the phase diagram of the system Si-Te is represented only one stable compound, Si_2Te_3, in the literature are reported other silicon tellurides: SiTe [35] and $SiTe_2$ [36]. Nevertheless, careful comparison of the optical and photoelectrical properties of single crystals of Si_2Te_3 [32] and crystals, to whom the formula SiTe [35] and $SiTe_2$ [37, 38] is ascribed, points out to their strong resemblance. These facts, and, also, the results of XRD on Si_2Te_3 reported in [129], allow to draw the conclusion that the SiTe and $SiTe_2$ crystals, previously studied, are identical to Si_2Te_3 with some deviations from the stoichiometric composition, either on the side of excess Si or on the side of excess Te.

References

[1] N. H. Abrikosov, V. F. Bankina, L. V. Poretskaia, E. V. Skundova, L. E. Shelimova, Semiconducting compounds their preparation and properties (russ.), Nauka, Moscow, 1967, 175 pages.
[2] N. H. Abrikosov, L. E. Shelimova, Semiconducting materials based on $A^{IV}B^{VI}$ compounds (russ.), Nauka, Moscow, 1975, 196 pages.
[3] Iu. I. Ravich, B. A. Efimova, I. A. Smirnov, Methods of semiconducting research in the application of lead chalcogenides: PbTe, PbSe and PbS (russ.), Nauka, Moscow, 1967, 384 pages.
[4] V. P. Zlomanov, A. V. Novoselova, p-T-x diagrams of state of the system metal-chalcogen (russ.), Nauka, Moscow, 1987, 208 pages.
[5] A. V. Novoselova, A. S. Pashinkin, Vapor pressure of the volatile metal chalcogenides (russ.), Nauka, Moscow, 1978, 112 pages.
[6] L. E. Shelimova, V. N. Tomashik, V. I. Gritsiv, State diagrams in the semiconducting materials research (systems based on Si, Ge, Sn and Pb chalcogenides) (russ.), Nauka, Moscow, 1991, 368 pages.
[7] M. A. Korjuev, Germanium telluride and its physical properties (russ.) Nauka, Moscow, 1986, 103 pages.
[8] V. V. Sobolev, Energy levels of the compounds $A^{IV}B^{VI}$ (russ.), Shtiintsa, Chishinau, 1981, 284 pages.
[9] G. Z. Vinogradova, Glass formation and phase equilibrium in chalcogenide systems (russ.), Nauka, Moscow, 1984, 174 pages.
[10] V. P. Zaharov, V. S. Gherasimenko, Structural peculiarities of the semiconductors in the glassy state (russ.), Naukova Dumka, Kiev, 1976, 280 pages.
[11] Iu. G. Poltavtsev, Structure of semiconducting alloys (russ.), Metallurghia, Moscow, 1984, 176 pages.
[12] A. Feltz, Amorphous and glassy inorganic solids (russ.), Mir, Moscow, 1986, 556 pages.
[13] D. I. Bletskan, Phonon spectra and electron phenomena in ordered and disordered germanium chalcogenides (Ph. D. hab. Thesis) /russ./, Kiev, 1984, 447 pages.
[14] M. Hansen, K. Anderko, Structure of double alloys (Two volumes); Vol. 2, Metallurgizdat, Moscow, 1962, 1488n pages.

[15] G. V. Samsonov, S. V. Drozdova, Sulphides (russ.), Metalurghiia, 1972, 303 pages.

[16] A. S. Berejnoi, Silicon and its binary systems (russ.), Izd. Akad. Nauk USSR, Kiev, 1958, 131 pages.

[17] H.-H Emmons, L. Theissen, Dampfahrungmessungen an Silicium chalkogenide, Monatsh. Chem., **103**(1), 62 (1972).

[18] H.-H. Emmons, L. Theisen, Ueber das Siliciummonoselenid, Z. anorg. Allg. Chem., , Band **361**(5-6), 321 (1968).

[19] E. S. Kohlmeier, H. W. Retzlaff, Ueber Aluminiumsulphide, Silizium sulphide und das System Al-Si-S, Z. Anorg. Chem. **261**, 248 (1950).

[20] W.C. Shumb, W. J. Bernard, The formation of silicon monosulphide, J. Amer. Chem. Soc., **77**(4), 904 (1955).

[21] H.-H Emmons, P. Hellmold, S. Moehlhenrich, Ueber die Chemie der Silicium-monochalkogenide, Z. Chem., 1975, Band 15, No. 7, S. 249-258.

[22] J. Peters, B. Krebs, Silicon disulphide and silicon diselenide: a reinvestigation , Acta Crystallogr. B **38**(4), 1270 (1982).

[23] M. S. Silverman, Soulen J. R., High pressure synthesis of new silicon sulphides, Inorgan. Chem. **4**(1), 129 (1965).

[24] J. E. Griffiths, M. Malyj, G. P. Espinosa, J. P. Remeika, Crystalline $SiSe_2$ and Si_xSe_{1-x} glasses: syntheses, glass formation, structure, phase separation, and Raman spectra, Phys. Rev. B, **30**(12), 6978 (1984).

[25] R. W. Johnson, S. Susman, J. McMillan, K. J. Volin, Preparation and characterization of Si_xSe_{1-x} glasses and determination of the equilibrium phase diagram, Mater. Res. Bull., **21**(1), 41 (1986).

[26] H. Gabriel, C. Alvarez-Tostado, Silicon disulphide and silicon diselenide, J. Amer. Chem. Soc., **74**(1), 262 (1952).

[27] R. Hillel, J. Cueilleron, Preparation et etude du seleniure de silicium: $SiSe_2$, Bull. Soc. Chim. France **15**(2), 394 (1971).

[28] A. Weiss, A. Weiss, Die Kristalstruktur des Siliciumdiselenids, Z. Naturforsch. B **7**(8), 483 (1952).

[29] L. G. Bailey, Preparation and properties of silicon telluride, J. Phys. Chem. Solids **27**(10), 1593 . (1966).

[30] B. Legendre, C. Souleau, C. Hancheng, N. Rodier, The ternary system gold-silicon-tellurium; a contribution to the study of the binary system silicon-tellurium and gold-silicon, and the structure of Si_2Te_3, J. Chem. Res. Synop., No. 5, 165 (1978).

[31] I. N. Odin, V. A. Ivanov, p-T-x diagram of state of the system Si-Te, J. Neorg. Chem. (russ.), **36**(5), 1314 (1991).

[32] K. E. Petersen, U. Birkholz, D. Adler, Properties of crystalline and amorphous silicon-telluride, Phys. Rev. B **8**(4), 1453 (1973).

[33] G. Exsteen, J. Drowart, A. Van der Auwera-Mahieu, R. Callaerts, Thermodynamic study of silicon sesquitelluride using a mass spectrometer, J. Phys. Chem. **71**(12), 4130 (1967).

[34] R. F. Brebrick, Si-Te system: partial pressures of Te_2 and SiTe and thermodynamic properties from optical density of the vapor phase, J. Chem. Phys. **49**(6), 2584 (1968).

[35] K. Smirous, L. Stourac, J. Bednar, Dire halbleitende Verbindung SiTe, Czech, J. Phys. **7**(1), 120 (1957).

[36] A. Weiss, A. Weiss, Siliciumchalkogenide, IV Zur Kentniss von Siliciumditellurid, Z. Anorg. Allg. Chem. **273**(3-5), 124 (1953).

[37] A. P. Lambros, N. A. Economou, The optical properties of silicon ditelluride, phys. stat. sol. (b) **57**(2), 793 (1973).

[38] J. W. Rau, C. R. Kannewurf, Intrinsic absorption and photoconductivity in single crystals $SiTe_2$, J. Phys. Chem. Solids, **27**(6/7), 1097 (1966).

[129] K. Ploog, W. Stetter, A. Nowitzki, E. Schoenherr, Crystal growth and structure determination of silicon telluride Si_2Te_3, Mater. Res. Bull. **11**(8), 1147 (1976).

[130] P. E. Gregoriades, G. L. Bleris, J. Stoemenos, Electron diffraction study of the Si_2Te_3 structural transformation, Acta Crystallogr. B **39**(4), 159 (1983).