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

Part. III Systems Sn-Chalcogenides

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The system tin-chalcogenides are reviewed from the point of view of the phase diagrams. Data on phase transitions are shown.

1.7 System Sn-S

The appearance of the gaseous phase for high sulphur concentration makes difficult the explanation of the phase equilibrium in the system Sn-S. In the paper [84] has been used thermal, chemical and X-ray diffraction methods of analysis, for the investigation of the equilibrium between solid, liquid and gaseous phases in the system Sn-S. The T-x projection of the p-T-x phase diagram of Sn-S has been studied in [85, 86] and is shown in Fig. 1.9. In the system Sn-S were revealed two compounds: SnS and SnS_2, which melt congruently. During the study of elasticity of SnS vapor, it was established that the melting point of SnS in a neutral atmosphere is 1153 ÷ 5 K, and the boiling point at normal air pressure is 1503 K. The maximum melting point (1154 ± 2 K) for SnS was found for sulphur pressure 3.34×10^3 Pa, and for SnS_2 (1143 K) for sulphur pressure of 4×10^6 Pa [84].

In the temperature interval 858 ÷ 875 K for SnS one observes an effect that corresponds to the polymorphous transformation [86, 89]. The studies of the phase transformations of the SnS crystals in the temperature range 295 ÷ 1000 K by XRD and neutron diffraction [87, 105], have shown that these crystals exhibit a structural transitions from low temperature α-phase (*B16* spatial group *Pbnm*) to high temperature β-phase with type II lattice (*B33*, spatial group *Cmcm*). The transition α→β is a second order transition of the displacement type. The transition is produced by the continuous shift of the Sn and S atoms along the axis [100]. The transition is related to the soft modes on the boundary of the Brillouin zone of the β-phase.

SnS_2, known as "plated gold", are golden-yellow platelets or scaly crystals shiny and very soft. As reported in [92], the dependence of the dissociation pressure of SnS_2 on the temperature is expressed by the equation:

$$\text{Lg p (Torr)} = [(4736+200)/T] + 6.88 \pm 0.15 \qquad (1.6)$$

SnS_2 is stable at room temperature in air, does not dissolve in water, decomposes in the royal water with the formation of tin chloride and release of sulphur, and, also, dissolves in sulphur solutions of the alkali metals and ammonium sulphate. By heating in air, SnS_2 completely transforms into SnO_2 [15].

Several researchers [84, 86, 93-95] supposed the formation of Sn_2S_3 and Sn_3S_4 by peritectical reaction. Based on X-ray diffraction, some authors support the opposite view regarding the existence of the intermediary compounds of tin sulphides. For example, in the paper [93] it is shown that between Sn_2S_3 and SnS does not exist any intermediary compounds. By using the same method of synthesis, the papers [85, 94] indicate the formation of the compound Sn_3S_4. The data reported by various authors are essentially different, also, both in the determination of the values of interplanar distances, intensity of the diffraction lines, and the ascribed Miller indices [86, 93, 95]. The NMR method has not confirmed the formation of the chemically ordered phases Sn_2S_3 and Sn_3S_4, because the spectra of both compounds are simply the superposition of the spectra of the

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individual compounds SnS and SnS_2 [91, 96]. The method of oscillation spectroscopy, also did not confirmed the existence in the Sn_2S_3 ($Sn^{2+}Sn^{4+}S_3$) and Sn_3S_4 ($Sn_2^{2+}Sn^{4+}S_4$) of the interatomic bonds determined by the hybridization of the tetravalent tin ions [10]. All the alloys, which contain from 40 to 50 at. % Sn, as e.g. the synthesized and carefully annealed Sn_2S_3 and SnS compounds, reproduce in all details the infrared transmission spectrum of the crystalline SnS [10]. The method of infrared spectroscopy, too, does not confirm the presence in the system Sn-S of the compounds Sn_2S_3 and SnS that have their own (different from SnS and SnS_2) crystalline structures and a system of bonds between different kind of atoms.

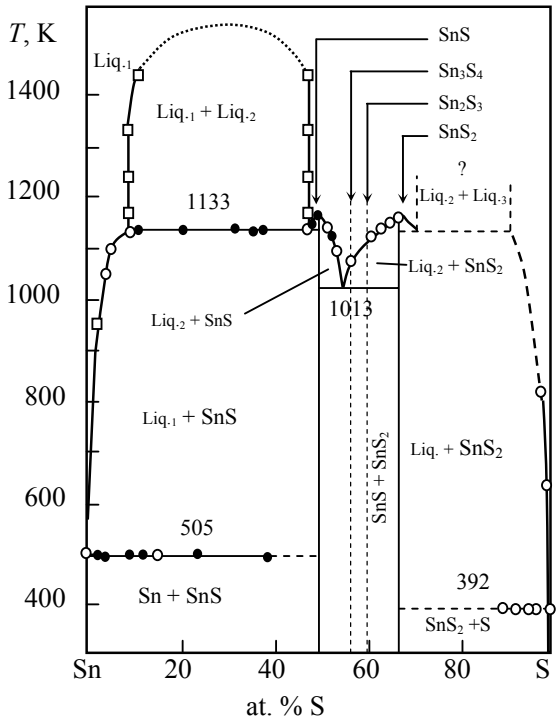

Fig. 1.9. The phase diagram of the system Sn-S [85].

On the tin side in the system Sn-S it exists a layering domain in the range 10-47 at. % S. The monotectic horizontal line corresponds to 1133 K, but layering is observed only up to 1523 K (Fig. 1.9). The second domain of layering in the liquid phase is fixed in the composition interval 70-90 at. % S. The eutectic between SnS and SnS_2 has the melting temperature 1013 K and composition 55 at. % [84].

As opposite to the antimony chalcogenides the tin chalcogenides are "one side" phases of variable composition. The domain of homogeneity of SnS is fully situated in the excess sulphur region (relative to the stoichiometric compound) [43, 85, 98, 99]. In Fig. 1.10 are given the boundaries of the homogeneity domain SnS, determined on the basis of Hall effect measurements and measurements of electrical resistance after annealing the $Sn_{1+\varepsilon}S$ samples in the temperature range 625 – 1010 K at fixed sulphur vapor pressure [85, 99, 112].

There was shown that SnS is not an exact stoichiometric compound, but contains sulphur excess, around 0.05 at. %. In the domain of homogeneity of SnS has been studied by chemical methods the sulphur vapor pressure at the temperatures 833, 880, 940, 1010, 1069 K and for various content of sulphur [98]. The analysis of these data has been carried out with the help of the equations that link vapour pressure, effective mass, density of states of electrons and holes, energy of formation, etc… The experimental points fit the calculated curves if one considers that the unique or dominant defects are doubly charged tin vacancies [V_{Sn}^{2+}], and the ionization energy of the Sn vacancies is 0.07 eV, while the energy corresponding to their association is $2\{V_{Sn}^{*}] \leftrightarrow [(V_{Sn}V_{Sn})^{*}]$ – 1.60 eV [112]. In the paper [98] are proposed other models of defects, e.g. single charged tin vacancies, but it is affirmed that they are less probable. The boundaries of the homogeneity domain

were estimated also on the basis of quasi-chemical approach by taking into account the neutral defects [V_{Sn}*] and the associations [$(V_{Sn}V_{Sn})^*$]. From Fig. 1.10 it is evident that the introduction of the electrically neutral defects shifts the boundary of the homogeneity domain on the side of higher concentration of super-stoichiometric sulphur atoms.

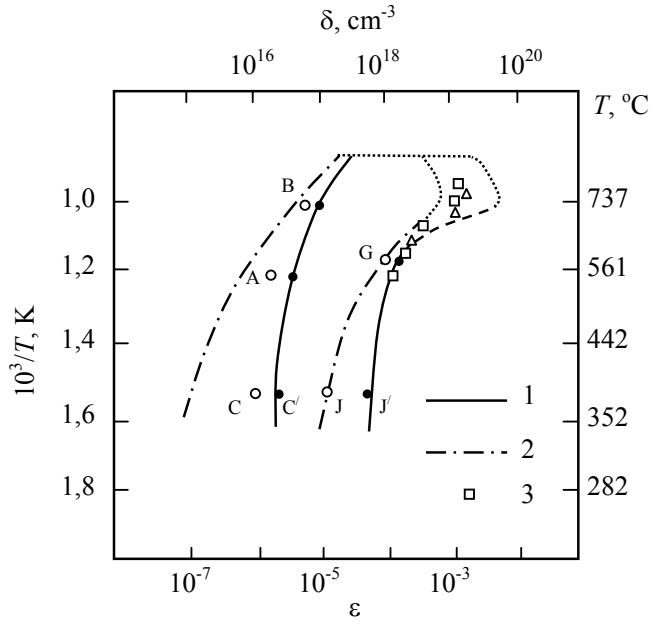

Fig. 1.10. The homogeneity domain of SnS [99] (ε is the excess of sulphur relative to the stoichiometry, at/mol). 1–calculation with the consideration, excepting the charged vacancy of tin, of neutral vacancies [V_{Sn}] and associates [$(V_{Sn}V_{Sn})^*$]; 2 – calculation with the measured data of Hall concentration holes (300 K) from the relation $V_{Sn}=p_x/2$; 3 – after [98].

1.8 System Sn – Se

The P-T-x phase diagram of the system Sn-Se is given in [100-102]. The T-x projection of this diagram is presented in Fig. 1.11, according to the data from the papers [103, 104]. In this system exists two chemical compounds: SnSe and $SnSe_2$. The above discussed supposition [14] on the existence in the system Sn-Se of the third compound, Sn_2S_3, based on the DTA data, has not been confirmed by XRD, NMR and microstructural investigations of this system [91, 96, 103]. The NMR spectrum of Sn_2S_3 represents a superposition of the spectra of SnSe and $SnSe_2$.

SnS melts congruently at 1153 ± 5 K [103]. The melting heat of SnSe is 32.63 ± 3.7 kJ/mol [102]. There are known two polymorphous modifications. The low temperature α modification (type B16) at 807 K transforms into high temperature rhombic β-modification of type TII (structural type B33) [105]. The phase transitions in SnSe are second order transitions [106, 107]. The transition α→β of the compound SnSe is of λ - type and occurs in an extended temperature interval, e.g. 200 K above the temperature of the phase transformation. At these temperatures takes place the shift of the atoms in the α-form only along the a-axis in the interval of coordinate $0 \le x \le 0.12$ and $0.48 \le x \le 0.50$ for selenium atoms. The structure of β-modification is derived from the NaCl type structure: the neighbouring octahedral layers with NaCl structure are shifted one to another by a/2. During the transition from α-form to β-form the coordination of all the atoms changes from three to two. Such phase transition is known as chemical reaction of the type S_{N2} [105].

The homogeneity domain of SnSe is situated in the range of selenium excess and its extension is 10^{-8} – 10^{-4} at. % Se [108]. From the results of Hall effect measurements in polycrystalline samples, annealed for various partial vapor pressure of Se in the temperature range 823-963 K, has been concluded that the defects responsible for the deviation from stoichiometry for high temperatures are the doubly ionized tin vacancies [V_{Sn}^{2+}]. The ionization energy of these

defects changes as a function of nonstoichiometry of the composition, in the range 0.012 – 0.20 eV. For low temperatures become essential the processes of association of the neutral vacancies $[(V_{Sn})^{*}]$: for the temperatures 663 – 713 K occur vacancy pairs $[V_{Sn})^{2*}]$, below 663 K one forms aggregates from four vacancies $[V_{Sn})^{4*}]$. The association energies of these complexes are 1.9 and 1.15 eV, respectively.

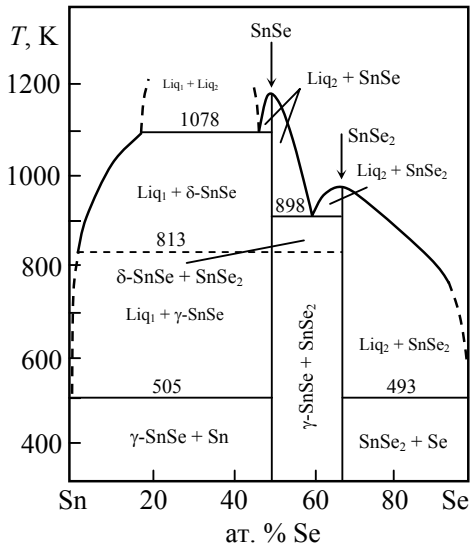

Fig. 1.11. Phase diagram of the system SnSe [103].

The sublimation and evaporation of SnSe take place incongruently, i.e. the composition of the vapor phase does not match that of the crystal. The incongruent sublimation of SnSe is indicated by the appearance after sublimation of the metallic tin in remainders, and, also, by the fact that in the vapor above the solid SnTe dominates the molecules SnSe, Se_2, $SnSe_2$ and, therefore, the vapor is enriched in selenium as compared to the solid phase of composition SnSe.

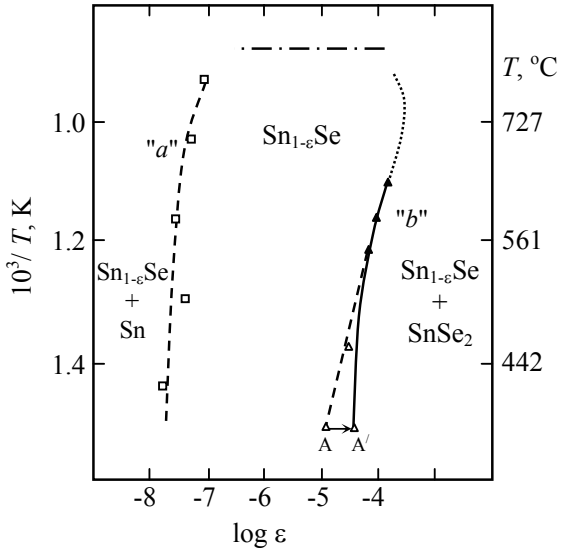

Fig. 1.12. The homogeneity domain of tin monoselenide [108]
(ε – selenium excess relative to stoichiometry, at/mol.).

Tin diselenide [103] melts congruently at 948 ± 5 K and 929 ± 2 K according to [100]. For $SnSe_2$ it is characteristic the presence of polytypism. Frequently one observes the polytypes 2*H*, 4*H,*

and 18*R* [110]. Indications on the boundaries of the homogeneity domain of $SnSe_2$ are lacking, but it is known that the crystals grown from the gaseous phase show electron type conductivity, while those grown from melt exhibit hole type conductivity [111, 164]. Moreover, during the growth of the $SnSe_2$ crystals from gaseous phase and from melt one forms different polytypes.

Using the DTA and XRD analysis methods on the tin side in the system Sn-Se has been revealed a large domain of layering (10 – 48 at. % Se). The monotectic horizontal line corresponds to the temperature 1078 K (Fig. 1.11).The eutectic between SnSe and $SnSe_2$ exhibits the melting temperature of 898 K and composition 61 at. % Se. The eutectic with initial components is degenerated.

On the basis of the eutectic SnSe + $SnSe_2$ it is possible to create single-layer heterostructures by the method of directional crystallization [97]. The layered eutectic SnSe + $SnSe_2$ consists of 10^3 – 10^4 heterotransitions/cm, in which the n-layer is $SnSe_2$, saturated by Sn, and the p-layer is SnSe with Se excess. The study of the corresponding relations between SnSe and $SnSe_2$ in heterostructures has shown that on the boundary of the section SnSe + $SnSe_2$ one observes the following relations: $(001)_{SnSe} \parallel (001)_{SnSe2}$ and $[110]_{SnSe} \parallel [1\,\bar{1}\,0]_{SnSe2}$.

1.9 System Sn – Te

The T-x projection of the P-T-x phase diagram of the system Sn – Te is shown in Fig. 1.13. In the system appears one chemical compound SnTe that melts congruently at 1079 K [14, 113, 114]. The maximum on the liquidus curve, corresponding to the point of congruent melting of SnTe corresponds to the composition 50.4 at. %Te [113]. The melting of SnTe is accompanied with the diminishing of the density: ρ_0(solid) = 6.15 g/cm^3, ρ_0(liq) = 5.87 g/cm^3, and crystallization enthalpy is ΔH_m = 1.9 ± 0.2 kJ/mol. [4].

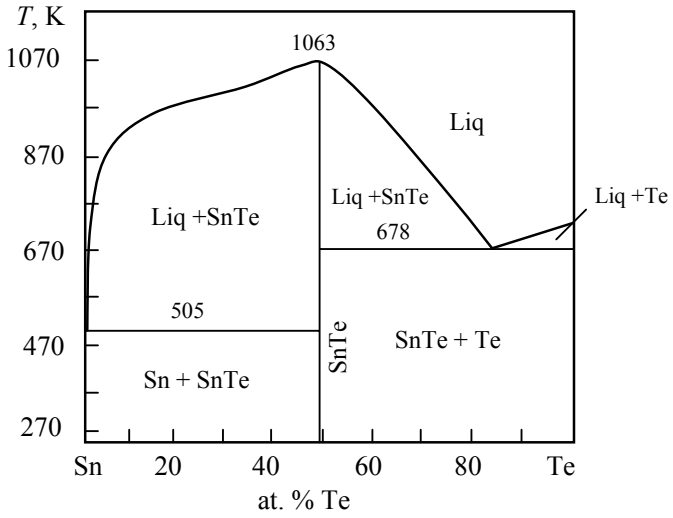

Fig. 1.13. Phase diagram in the system Sn–Te [114].

SnTe sublimates incongruently. Because the vapor consists basically in SnTe molecules and a small quantity of Sn, that is released by sublimation (less than 0.3 wt. % for the sublimation of 95 % of the sample), then the sublimation can be regarded as quasi-congruent [4]. SnTe forms with tellurium an eutectic with the coordinates: 85 at. % Te; T_e = 678 K. In the composition domain Sn – SnTe the eutectic is degenerated. The solubility of tellurium in tin at 103 K is around 0.11 at. %.

As a result of many investigations on the homogeneity domain of SnTe [109, 114-121], performed with different methods, it has been established that SnTe has an one side domain of homogeneity (Fig. 1.14 a), shifted towards the Te excess side, with ~1 at. % Te. The maximum on the melting curve corresponds to the composition 50.4 at. % Te. The most experimental data and

theoretical calculations of the boundary of the homogeneity domain [120, 121] is related to the temperatures above the temperature of eutectic transformation in the system Sn-Te on the side of Te (~678 K) [113]. From this follows that in the interval from 678 K to ~1000 K the width of the homogeneity domain practically does not change and its boundary corresponds to the composition ~50.1 and 50.9 at. % Te. Only in the paper [114] it is shown that for lower temperature (573 K) the boundary of the homogeneity domain on the tellurium side shifts towards the diminishing of the deviation from stoichiometry. It is necessary to remark that on the extended domain of homogeneity essentially influences the high temperature homogenization annealing [117].

Deviation from stoichiometry implies a high concentration of own lattice defects. According to the results of measurements of concentration dependence of the lattice parameters, of the picnometric density and partial vapor pressure of tellurium in the range of homogeneity domain it has been concluded that the dominant defects in SnTe are the cation vacancies [113, 114], although in [116] has been established the existence of the antistructural defects. In the range of the homogeneity domain of SnTe has been observed a non-monotonous dependence of the properties on composition and the presence of special points on the curves composition – property at 50.4 at. % Te: maximum thermo-emf coefficient (α), fracture on the microhardness curve (H), maximum deviation from the Végard law on the curve of lattice parameters (a), strong diminishing of the rate of Hall constant fall (R_x) after 50.4 at. %. Te The non-monotonous character of the dependencies of the properties on concentration has been related [117, 118] to the simultaneous action of minimum two factors: the increase of the concentration of cation vacancies and the processes of their interaction. The last factor stimulates the processes of redistribution of the tin vacancies on the cation sublattice (e.g. formation of super-structural vacancies), and, as a result, in the range of the homogeneity domain exist two subdomains of composition (50.1 – 50.4 and 50.6 – 50.8 at. % Te) with different vacancy concentration and different character of their distribution. An additional argument in the favor of this conclusion is the results of investigation of microhardness and of Mössbauer spectra ^{119}Sn of the SnTe samples, where the tellurium content varied from 49.9 to 51.5 with 0.5 % steps [119]. For the increase of tellurium content the isomer shift decreases and on the curves of concentration dependencies of the half-width of the Mössbauer line (Γ) and of the area below (S), and, also, microhardness (H) one observes a maximum at 50.4 at. % Te (as narrow maximum) and fracture, respectively.

On the basis of investigation of solid and liquid phase in the system Sn-Te there were determined the thermodynamical functions of vacancy formation of different components in the compound SnTe. By using the obtained data, the authors of [120], calculated, with the consideration of the change of the activity of the components in the equilibrium liquid phase, the limit concentration of the point defects and have built the homogeneity domain for Sn-Te in the range 573 K – T_{melt} (Fig. 1.14 b). In the tin telluride crystals, obtained from melt, both on the left and right side of the phase diagram of Sn-Te, in all the temperature range dominates the concentration of tin vacancies, that leads to crystals of only p-conductivity.

The tin telluride exhibits a phase transition from low-temperature rhombohedral lattice (α) to the high-temperature phase of NaCl-type (β) [122, 123], whose temperature strongly depends on the degree of deviation from stoichiometry [124]. In tin telluride with weak deviation from stoichiometry, characterized by hole concentration $p \sim 1.2 \times 10^{20}$ cm^3, the phase transition $\alpha \rightarrow \beta$ takes place at 97.5 K [125]. The study of the dependence of the critical temperature of the phase transition of the displacement type on the concentration of the charge carriers in single crystals of p-SnTe has shown that T_c smoothly diminishes with the increase of p in the hole concentration domain $p = (1.2 – 2.7) \times 10^{20}$ cm^{-3} and tends to zero at $p = 1.3 \times 10^{21}$ cm^{-3}. The theoretically obtained dependence $T_c(p)$ in the frame of the model of electron interaction with transversal optical phonons with the constant of the optical deformation potential: 9.1 eV, coincides with that experimentally measured curve. The study of the phase transitions in SnTe (with charge carrier concentration 2×10^{20} cm^{-3}) with the method of Mössbauer spectroscopy, in the temperature range 8-300 K has allowed to the authors of [123] to clarify the existence of a still one structural phase transition at 160 K.

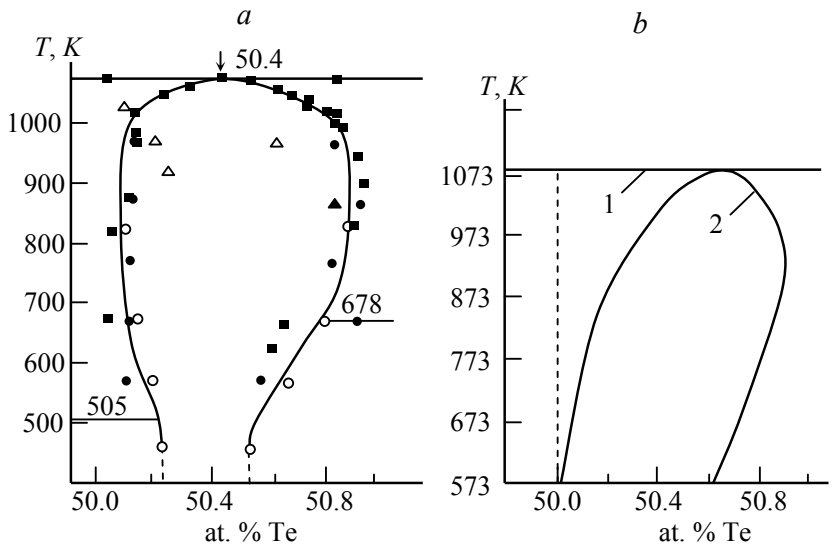

Fig. 1.14. *a* – Phase diagram of the system Sn–Te in the domain of the compound SnTe [117]; *b* – the calculated boundaries of the homogeneity domain of tin telluride in the system Sn–Te (1 – liquidus, 2 – solidus) [120].

The analysis of the above described phase diagram of the system A^{IV}-B^{VI} permits to determine some basic tendencies at the change of the atomic number of the metal and/or chalcogen. During the increase of the atomic number of the metal or chalcogen the phase diagram of the system takes a more simple feature: it is diminished the tendency to layering in the liquid state, and, also, the number of compounds, formed in the systems, and their stability increases. Thus, in the systems Ge-S(Se) and Sn-S(Se), without monochalcogenides, one forms stable, congruently melting di-chalcogenides. In the systems A^{IV}-Te, monotellurides do appear. In general, one observes the following basic tendency: when the atomic number of the metal and/or chalcogen increases one observes a transition from the formation of compound with different stoichiometries and complex crystalline structure with predominant covalent component of the bond to the formation of compound with more simple stoichiometry and structure with significant contribution of ionic and metallic component of the bond [6].

The above considered peculiarities of phase formation with variable composition based on a compound of the type A^{IV} B^{VI} lead to the fact that crystals, grown by Czochralski or Bridgman methods from melt, close to the stoichiometry, usually exhibit a determined type of conduction and enough high concentration of charge carriers, conditioned by the presence of high amount of point defects in the structure. The effective means of controlling the properties of such crystals is their last annealing at determined temperatures and in controlled vapor atmosphere of the components that constitute the compound.

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