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MATERIAL SYNTHESIS AND GROWTH OF THE SINGLE CRYSTALS OF THE TYPE $A^{IV}B^{VI}$ AND $A^{IV}B_2^{VI}$

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The synthesis and growth of single crystals of the type $A^{IV}B^{VI}$ and $A^{IV}B_2^{VI}$ are discussed. The synthesis of germanium, silicon and tin chalcogenides, the preparation of single crystals from melts and growth of single crystals from the gaseous phase are analysed in detail.

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1. Introduction

The technology of the semiconducting compounds is at variance with the technology of the elementary semiconductors due to the presence of the synthesis process. This process consists in the formation of the compounds as a result of the development of various kind of chemical reactions.

2. The synthesis of germanium, silicon and tin chalcogenides.

The synthesis of the semiconducting compounds $A^{IV}B^{VI}$ and $A^{IV}B_2^{VI}$ is achieved by direct and indirect methods If the initial materials used for synthesis represent components of the compound in the elementary form, then the method belongs to the category of the direct methods. The main features of this method are: a) the simplicity to maintain the stoichiometry in the synthesis process and the absence of component losses; b) not complicated apparatuses; c) lacking of side materials and component excess that determines the high purity of the obtained product. In the direct synthesis the interaction of the components takes place after the reactions that exhibit diffuse or kinetical character. The second order reactions, that use the kinetic interactions of the initial components, find the most applications in the technology of the compounds of the type $A^{IV}B^{VI}$ and $A^{IV}B_2^{VI}$. The compounds are obtained by melting the initial components. The material is got by the interaction of the vapors of the volatile component with the melt of the non-volatile or vapors of the components.

According to [1-13], the calculated weight of the corresponding elementary materials of total mass 25 – 30 g are introduced in cylindrical glass ampoules, purified mainly by chemical – thermal processing, of length 15 – 20 cm and with the internal diameter of 1.8 – 2.2 cm. The charged ampoules are evacuated down to a residual pressure of ~133 Pa, sealed and put in an electrical furnace. Because sulphur and selenium exhibit high volatility, for synthesis it is necessary to take into account the dependence on temperature of the vapor pressure in order to avoid the explosion of the ampoule. With the aim to establish the temperature of the interaction reaction of the germanium with sulphur and selenium, the authors of [14] carried out the thermal analysis of the synthesis process. The reaction of germanium with sulphur and selenium shows a complicated exothermal character. The interaction with sulphur takes place in the temperature range 680-928 K, and with selenium in the interval 820-863 K. Based on these data the synthesis regime of the tin mono- and di-chalcogenide is established. For the one temperature synthesis it is necessary to use a two-stage method. In the first stage the charged ampoules are heated with the rate of 3-4 K/s up to 820-850 K, maintaining the ampoule at this temperature for 12-15 h, thereafter the temperature is increased with the rate of 2-3 K/min up to the complete melting of the charge. At this temperature the ampoule is maintained 24 h with the aim to finish the synthesis and to reach a good homogeneity of the melted material. After that, the ampoule is cooled together with the

furnace or is quenched in air. During synthesis the melt is homogenized by vibrational mixing. The use of forced vibrational mixing at synthesis of the silicon, germanium, and tin chalcogenides, compared with traditional convective melting of the components, has the following advantages: it disappears the necessity of milling the components before charging the first layers for crystal growth and this decreases the probability of impurification of the obtained crystals with off side additions; it is improved the synthesized materials (the unreacted components are lacking, increases the homogeneity of the melt).

The second, combined method that is applied especially for the synthesis of binary sulphide and selenides consists in the following. In the first stage the evacuated and sealed ampoules with the length of 20-22 cm are put in a tubular inclined or vertical electro-furnace, so that part of the ampoule (3-5 cm) remains in air. The temperature in the furnace, where is situated the bottom part of the ampoule with the material, is raised above the melting temperature of the material to be synthesized. At this temperature parts of the sulphur (selenium) vapors react with the metal, and parts condense in the cold end of the ampoule, but as a consequence of its inclination the position of the condensed material is flowing again in the region of the reaction. During the developing of the reaction the ampoule is introduced in furnace so that at the end of the reaction, when the sulphur (selenium) vapors disappear, the whole ampoule will sit in the furnace. In the second stage the furnace is transposed in vertical position and the melt is obtained in the one-temperature synthesis regime.

The group of indirect synthesis consists in the methods, where the initial material represents a chemical compound that is a component of the final semiconducting compound. The interaction of the initial material develops in this case by reactions of the type: oxidation-reduction, substitution, exchange, disproportion, etc. The indirect synthesis methods are developed at temperatures bellow the melting point of the syntesized compound. Let it see examples of preparation of the germanium chalcogenides by the indirect methods with the use of the chemical reactions of different type [15].

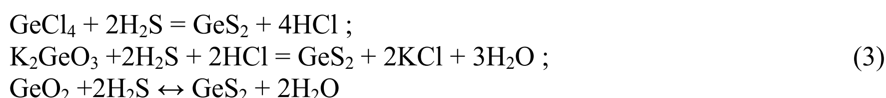
Germanium mono-sulphide is prepared by passing H_2S gas flux on the weakly oxidized solutions of di-valency germanium salts, e.g. through the reaction:

$$GeCl_2 + H_2S \leftrightarrow GeS + 2HCl \qquad (1)$$

Under the action of sulphur the germanium hydride is transformed by heating it in germanium di-sulphide GeS_2:

$$GeH_4 + 4S \leftrightarrow GeS_2 + 2\,H_2S \qquad (2)$$

The germanium di-sulphide is obtained, also, by passing H_2S on acid solution (pH<2) of a salt of the four-valency germanium or by oxidizing the solution of thio-germanides of alkali-earth metals. The synthesis can be done with a dried method, by heating GeO_2 in a H_2S flux up to 1070 K:



$$\begin{aligned} &GeCl_4 + 2H_2S = GeS_2 + 4HCl\ ; \\ &K_2GeO_3 + 2H_2S + 2HCl = GeS_2 + 2KCl + 3H_2O\ ; \\ &GeO_2 + 2H_2S \leftrightarrow GeS_2 + 2H_2O \end{aligned} \qquad (3)$$

GeS_2 is a white crystalline powder with the density: 3.03 g/cm^3. It has low solubility in water and slowly hydrolizes. For strong heating evaporation, the heating in air transforms the compound in GeO_2 and SO_2. The GeO_2 is reduced with hydrogen to GeS in the temperature range 720 ÷ 750 K. The GeS is formed during heating GeS_2 with crystalline germanium in CO_2 flux. The heating of of GeS_2 with HNO_3 or H_2SO_4 leads to the exchange of sulphur by hydrogen and the transformation in GeO_2. The germanium di-sulphide easily is dissolved in NH_3, ammonium sulphide, sulphides and poly-sulphides of the alkali metals.

Tin monosulphide is obtained by heating the metallic tin in a H_2S or with tin penta-sulphide, and, also, by the interaction of sulphur with the molten $SnCl_2$:

$$Sn + H_2S = SnS + H_2 \qquad (4)$$

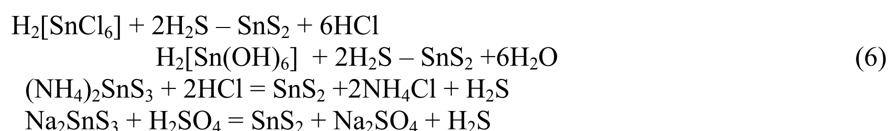
By passing gaseous H_2S on the weakly oxidized solutions of salts of di-valent tin in the absence of air, is precipitated tin mono-sulphide:

$$SnCl_2 + H_2S = SnS + 2HCl \quad (5)$$

The tin mono-sulphide decomposes, by heating in vacuum, in SnS_2 and Sn, exhibit low solubility in water, ammonia, carbonate and sulphide ammonium, in diluted solutions of alkaline metals, but shows good solubility in concentrated acids (e.g. HCl), in yellow ammonia polysulphide and in concentrated alkaline and sulphides of alkali metals (in the presence of oxygen).

The tin di-sulphide is prepared by heating metallic tin or tin di-oxide with sulphur in the presence of ammonium chloride. An amalgam of tin is prepared by mixing 12 weight parts of metallic powder with 6 weight parts of mercury in a porcelain mortar.

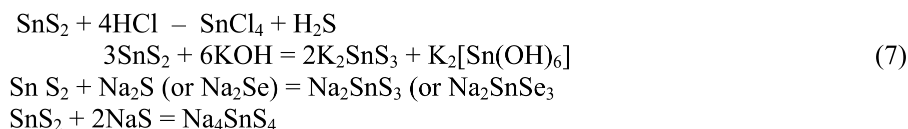
If H_2S is introduced on the acid solution of $SnCl_4$ (2.28 n HCl, pH ~0.5) or on water suspension of $H_2[Sn(OH)_6]$ acid, one gets tin di-hydrate di-sulphide: $SnS_2 \cdot 2H_2O \cdot OH$. The di-hydrate is obtained, also, by the oxidation of a diluted solution of thio-stannate. The di-hydrate heated at 310 K transforms in $Sn_2S_2 \cdot H_2O$, and up to 1000÷1020 K in H_2S flux, in the golden crystalline modification.



$$\begin{aligned} &H_2[SnCl_6] + 2H_2S - SnS_2 + 6HCl \\ &H_2[Sn(OH)_6] + 2H_2S - SnS_2 + 6H_2O \\ &(NH_4)_2SnS_3 + 2HCl = SnS_2 + 2NH_4Cl + H_2S \\ &Na_2SnS_3 + H_2SO_4 = SnS_2 + Na_2SO_4 + H_2S \end{aligned} \quad (6)$$

Tin disulphide hardly dissolves in water, ammonium carbonate and diluted acids. During heating SnS_2 reacts with chlorine and iodine, and form tin chloro- and iodine-sulphides: SnS_2SnCl_4 and SnS_2SnI_4. If SnS_2 is heated in air, it appears SnO_2 and SO_2.

The compound SnS_2 dissolves in concentrated HCl, in aqua regia, alkali, concentrated NH_4OH, and in alkali selenides:



$$\begin{aligned} &SnS_2 + 4HCl - SnCl_4 + H_2S \\ &3SnS_2 + 6KOH = 2K_2SnS_3 + K_2[Sn(OH)_6] \\ &Sn\,S_2 + Na_2S \text{ (or } Na_2Se) = Na_2SnS_3 \text{ (or } Na_2SnSe_3 \\ &SnS_2 + 2NaS = Na_4SnS_4 \end{aligned} \quad (7)$$

3. The preparation of single crystals from melts

One of the main causes of the technological difficulties of the growth of the Si, Ge and Sn chalcogenides is the existence of many polytypes and polymorphs of these compounds. For crystal growth one uses very different methods that determine, on one hand, the multi-facetted physico-chemical properties of the semiconducting materials, and, on the other hand, determine the particular method for preparing the material with pre-established properties.

The methods of crystal growth, usually are classified after two main characteristics:

1). The phase state and the component of the initial material
2). The driving forces

According to the first principle the following group of methods exist:

- growth from stoichiometric melts;
- growth from solutions
- growth from gaseous phase.

The classification of the methods in the limit of the above main groups is made after the character of the driving force. The driving forces of the growth process are the temperature gradient, pressure, concentration or chemical potentials. Therefore, every known growth method is based on the maintaining during growth of an optimal value of the gradient of one from these parameters, usually the temperature.

Let us see the basical principle of the methods of growth of the layered chalcogenide of the crystals from the IV-th group from melt and gaseous phase. The growth of crystals is determined by the conditions of the phase transitions, which ensure the production of single crystals with given composition and properties.

Method Bridgeman – Stockbarger. Single phase, single crystal ingots of the $A^{IV}B^{VI}$ compounds are obtained by directional crystallization, by moving down the ampoule containing the melt in the cold region of the vertical tubular furnace. This method is enough simple and gives the possibility to get relatively large crystals. For the growth of crystals by this method there are used vertical growth furnace, consisting in two independent zones that permit to change the longitudinal temperature gradient in the necessary limits and to make the heating in the most acceptable conditions . For the shift of the crystallization front it is used a special up-raising mechanism, that permits to move the furnace or the ampoule with the material. As growth containers are used quartz ampoules with conic basis or with an elongation in the bottom part, as a capillary with the diameter of 2 ÷3 mm and length of 10 ÷15 mm (Fig. 1 a).

The quartz ampoule that contains the initial material is sealed at the upper end to the quartz support and is put in the upper high temperature region of the furnace. After the melting of the material in the quartz ampoule and maintaining there for a short time, it is connected the mechanism that moves the support, and the ampoule enters gradually within the low temperature region. In order to reduce the convection and the radiation within the furnace, and, also, for reaching a more narrow change of the temperature gradient, the regions of the furnace must be separated by a diaphragm. The electrical power must be stabilized. In many cases this is enough for maintaining the temperature regime. The oscillation of the electrical power increases and decreases the temperature in both furnaces, and, as a consequence, the crystal growth rate changes. This can lead to the formation of crystal imperfections and compositional non-homogeneities, especially in the case of the growth of mixed or doped crystals. That is why, for growing more perfect crystals it is necessary to regulate carefully the temperature. Because the driving force of the process of crystal growth by this method is the temperature gradient on the boundary between phases, the value and the form of this gradient determine the rate and position of the crystallization front. If the crystallization front is concave (for example in the case of somewhat rapid descending of the ampoule), then the cooling through the lateral surface leads to the formation of random nuclei and the ingot passes in the polycrystalline state.

Huang et al. [371] have studied the form of the crystallization front during the growth of $Sn_xPb_{1-x}Te$ by the method of vertical directional crystallization. Crystals of solid solutions with the diameter of 16 mm have been grown in quartz ampoules with the rate of 3 mm/h after maintaining the melt for homogenization at 1273 K for 18 h. For evidencing the form of the crystallization front, the ampoules with the growing crystal have been quenched in water. The crystallization front has been evidenced on longitudinal sections of the ingot by electrochemical pickling. The change of the composition in the vicinity of the crystallization front has been determined with microsonde analysis. The construction of the furnace permitted to change the form of the crystallization front from concave to convex. The thickness of the boundary diffusion layer near the crystallization front is 40 – 90 μm. The not too large thickness of the diffusion layer indicates a convective mixing of the melt for temperatures gradients close to the crystallization front in the range 22 ÷55 K/cm.

Many investigations [1, 10, 17, 13, 14, 16] have shown that for the growth of hard mono-crystals GeS, GeSe, GeS_2, $GeSe_2$ Si_2Te_3, $PbGeS_3$ and Pb_2GeS_4 the optimal conditions are: the velocity of moving the crystallization front 0.01 – 0.02 mm/h, and the temperature gradient in the crystallization region 3÷5 K/mm (Table 1). The use of such low velocities of ampoule movement ensures the complete development of the peritectic reaction, even in the case of the preparation of mono-crystals, of incongruently melting compounds, e.g. GeSe. The general feature of the GeS and $GeSe_2$ crystals, got by Bridgeman – Stockbarger method is represented in Fig. 1.

Table 1 The conditions for the growth of $A^{IV}B^{VI}$ and $A^{IV}B_2^{VI}$ crystals from melt.

Compound	Method of growth	Temperature of the melt (K)	Temperature gradient ΔT (K/cm)	Drawing speed of the ampoule (cm/h)	Crystal shape	Crystal size (mm)	References
GeS	Bridgman	980	20 ÷ 30	0.015 ÷ 0.02	Cylinder	Diameter - 12 ÷ 15, Length - 40 ÷ 50	[1]
α-GeS_2	Bridgman	1150	30 ÷ 60	0.015 ÷ 0.02	Cylinder	Diameter - 12 ÷ 15, Length - 30 ÷ 40	[6,18]
$GeSe_2$	Bridgman	1080	10 ÷ 40	0.01 ÷ 0.05	Cylinder	Diameter - 15,	[10-14]

						Length - 50 ÷ 60	
Si_2Te_3	Bridgman		50	0.3	Cylinder	Diameter - 20	[17]
4H – SnS_2	Bridgman			0.02 ÷ 0.08	Cylinder		[19]
2H – SnSe	Bridgman		180	0.2	Cylinder	Diameter - 10, Length - 20 ÷ 30	[24]
$Sn_xPb_{1-x}Te$	Bridgman		12	0.12	Cylinder	Diameter - 10, Length - 70 ÷ 80	[25]
$Sn_xPb_{1-x}Te$	Bridgman		3,5	0.04	Cylinder	Diameter - 16	[22]
$PbGeS_3$	Bridgman	900 ÷ 910	20 ÷ 60	0.014 ÷ 0.04	Cylinder	Diameter - 15 ÷ 20, Length - 60 ÷ 70	[26]
Pb_2GeS_4	Bridgman	930 ÷ 940		0.014 ÷ 0.04	Cylinder	Diameter - 15 ÷ 20, Length - 60 ÷ 70	[26]

Compound	Method of growth	Atmosphere, flux	Temperature of the melt (K)	Drawing speed of ampoule (mm/h)	Turning speed of ampoule (turns/min)	Crystal shape	Crystal size (mm) Weight (g)	References
GeTe	Czochralski	Inert gas 13 atm.; B_2O_3				Cylinder	Diameter - 25, Length – 70 Weight - 125 ÷ 150	[28]
GeTe	Czochralski	Ar or He 3 atm.	998	25 ÷ 75	15	Cylinder	Diameter:9.5, Length – 150 Weight - 200	[29]
SnTe	Czochralski	He, 300 Torr B_2O_3		30	15	Cylinder	Diameter - 20 ÷ 22, Length - 40	[31]
SnTe	Czochralski	Ar or He 3 atm.	1078	25 ÷ 75	15	Cylinder	Diameter 9.5, Length – 150 Weight - 200	[29]
PbTe	Czochralski	N_2, 1 atm.; B_2O_3					Diameter - 25, Length - 75	[34]
$GeSe_2$	Czochralski	vacuum B_2O_3	1013	10	13	Plastic	10×0.8×0.2	[30]
$Sn_xPb_{1-x}Te$	Czochralski	Ar, 0.7 atm., B_2O_3		0.8 ÷ 3	20	Cylinder	Diameter- 18, Length – 200 Weight - 300	[30]
$Sn_xPb_{1-x}Te$	Czochralski	B_2O_3		0.01 ÷ 0.1		Cylinder		[22]

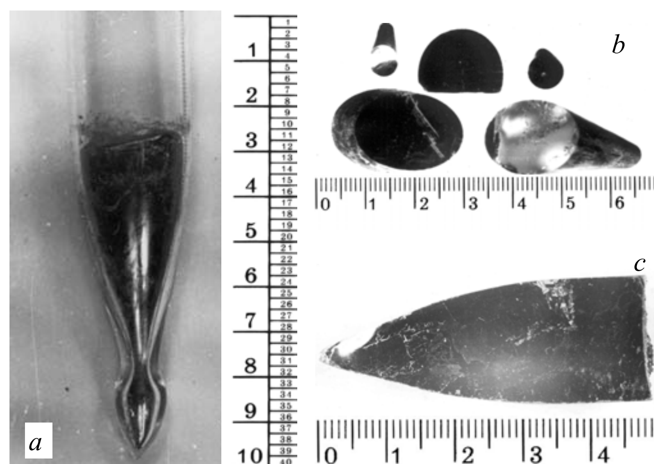


Fig. 1 General feature (a) and natural fractures (b, c) of the monocrystals of GeS (a, b) and $GeSe_2$ (c) obtained with the method of Bridgmann – Stockberger [13].

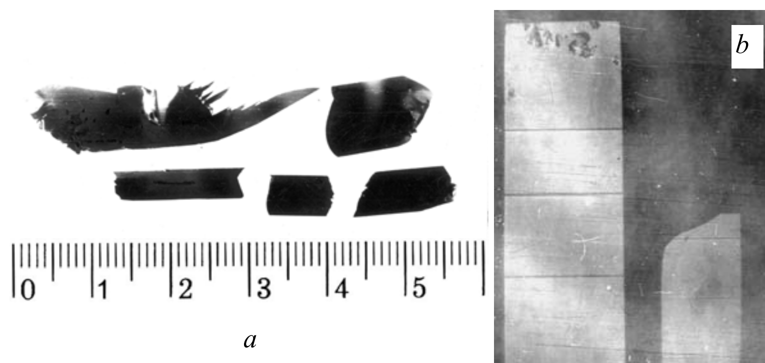


Fig. 2 Various forms of crystallization of GeS and GeSe, obtained from gaseous phase: [1]. a – platelet-like b. lenticular

The crystals of germanium and tin mono-chalcogenides, obtained from stoichiometric melt and doped by various additions, show hole conductivity [1, 9]. Only in one paper it was shown that during the introduction of Sb in the SnSe melt, it is possible to get samples with n-type conductivity.

By changing the shape bottom of the ampoule, where the mono-crystals of SnS_2 are grown by the Bridgeman method with the rate of 0.02 – 0.08 cm/h, it is possible to get crystals of various orientations: from that corresponding to c-axis perpendicular to the direction of the growth (at the regular capillary end), to the axis *c*, parallel to this direction (at the plane bottom of the ampoule) [19]. For other shape of the ampoule are got intermediary orientations. The type of packing of the layers –S-Sn-S- during the growth from melt depends on the direction of the axis *c*. In the crystals with axis *c* perpendicular to the direction of growth, the layer packing corresponds to the 4H polytype, parallel to this direction – is a packing of higher order, for intermediary directions, the packing type depends on the rate of growth.

Enough rarely is used the Czochralsky method (pulling from melt) [30-34] for the preparation of chalcogenides mono-crystals of the fourth group. The scheme is given in Fig. 3. The main difficulty is to ensure the maintaining of the stoichiometry of the melt for high vapor tension of the chalcogen and rather high free volume. In order to prevent the evaporation of the melt in the Czochralski method one gives an excess of pressure with an inert gas. As buffer it is used B_2O_3 (as a film on the surface of the melt), which gives inertness relative to melt and enough low melting temperatures, specific weight and vapor tension.

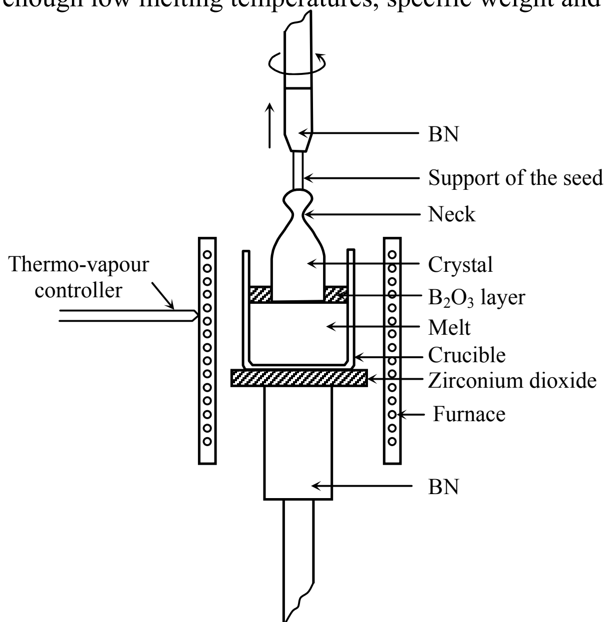


Fig. 3 The general scheme of the drawning of $A^{IV}B^{VI}$ crystals with a Czochralski method.

In the papers [16, 22] the authors used the method of capillary regulation during the drawing of the PbTe crystals and of solid solutions $Sn_xPb_{1-x}Te$ from melt. The essential feature of the procedure consists in the fact that during the growth of the crystals by Czochralski method, in the melt is introduced the end of the thin capillary, where it is put part of the melt. The final ball formed after hardening is used in the next drawing. The necessary condition for the application of this method is the chemical inertness of the capillary material relative to melt and atmosphere, where the growth is conducted. This condition is achieved by Ta and Ta-Nb capillaries for the growth of the crystals SnTe, PbTe and $Sn_xPb_{1-x}Te$. There were investigated the peculiarities of the growth of the drawing material during the starting period of the process, conditioned by the local distortion of the thermal field by the capillary near the surface of the melt. This method is effective during the growth of the compounds for which it is difficult to get qualitative crystals, especially for solid solutions. By Czochralski method are obtained single crystals of composition $Sn_xPb_{1-x}Te$ (x=0.25) with the weight up to 70 g, length up to 100 mm and a diameter up to 15 mm, p-type conductivity, with concentration of the major charge carriers ~(1 – 5)×10^{19} cm^{-3}. The density of the picklimg wells in the obtained mono-crystals has been enhanced from 4×10^4 cm^{-2} in the region of pickling till 10^6 cm^{-2} in the bottom part of the ingot.

The shortcomings of the growth method for the $A^{IV}B^{VI}$ and $A^{IV}B_2^{VI}$ crystals from melt are: low velocity of this process, the necessity to use high temperatures that lead to the increase of the defect concentration (vacancies and dislocations) in the crystals, the localization in the crystal of all the impurities from the initial materials. Therefore, during the development of the technology of crystal growth for $A^{IV}B^{VI}$ and $A^{IV}B_2^{VI}$ compounds there was paid high attention to the methods of their preparation from the gaseous phase.

4. Growth of single crystals from the gaseous phase.

The growth of crystals from the gaseous phase can be performed at significantly lower temperatures, essentially bellow the melting temperatures of the material. This means that the concentration of vacancies and dislocations in the crystal can be diminished to a minimum (the vacancy concentration depends exponentially on temperature). Apart this, the methods of low temperature crystallization are the most acceptable for getting crystals of materials that melt incongruently and, also, materials with tendency towards polymorphism, when it is necessary to get crystals of low temperature polymorphous modification. The other advantage, due to choosing the method for getting chalcogenide monocrystals of the IV-th group, is related to the enough high vapor pressure, therefore the mass transport through the gaseous phase is easily achieved.

The growth of crystals $A^{IV}B^{VI}$ and $A^{IV}B_2^{VI}$ from the gaseous phase is performed by several methods, which conventionally can be divided in two classes: methods based on pure physical condensation, and methods, that suppose the participation of a chemical reaction whose product is the crystallized material. In the first class, the most important is the method based on the process of sublimation-condensation, and the second class is based on methods of chemical synthesis in the crystallization region on the account of decomposition (or activation) of the gaseous chemical compounds and chemical transport.

Sublimation-condensation method. The growth of the chalcogenide crystals of the IVA subgroup with the sublimation-condensation method was conducted in closed or flowing systems [7 – 12, 35-43]. A closed system can be obtained in sealed quartz ampoules. In this method the initial material is the polycrystalline ingot of the compounds $A^{IV}B^{VI}$ and $A^{IV}B_2^{VI}$. The sublimation method can be achieved in two different versions. In the static method the initial polycrystalline material sublimates in the sealed quartz ampoule, primarily evacuated or filled by inert gas. As a function of gaseous medium the mass transport in closed systems is achieved by molecular beams (in vacuum) using the molecular or convective diffusion.

For the growth of the germanium and tin chalcogenides after the method of statical sublimation, the sealed ampoule containing the polycrystalline material is put in a horizontal two-zones furnace. Firstly both zones are heated up to the temperature with 30 ÷ 40 K below the melting temperature of the material; it is established the pressure of the saturated vapors, corresponding to this temperature. Thereafter, the temperature of the second region of the furnace, where is situated the empty part of the ampoule is diminished to a lower temperature, T_{cond}. As a consequence of the difference in the vapor pressure takes place the transport of the initial material from the hot zone to the cold zone, where it occurs the condensation as monocrystals. It was established that by crystallization, as phase transition, the new phase forms not immediately reaching the thermodynamical equilibrium (saturation), but only in the systems with drying. In the static method of getting crystal by sublimation, the drying is achieved by the temperature difference (ΔT) between the zones of evaporation and condensation (the values T_{evap} and T_{cond} are given in Table 2). It is necessary to remark that for

the horizontal position of the ampoule, it is very difficult to ensure a narrow boundary between the regions of evaporation and condensation. When we go from the evaporation to condensation zone the level of saturation increases continuously. Thus, in the horizontal ampoule there are separated, spatially divided zones, where the saturation has different magnitude. Therefore, the formation of separate nuclei (germs) or their conglomerates is produced in different parts of the ampoule. During the growth of the Ge and Sn chalcogenide mono-crystals by the method of static sublimation in the absence of added materials , i.e. in the conditions of spontaneous crystallization, as a function of crystallization conditions (saturation, impurities, gasodynamics) one forms platelet and lenticular crystals (Fig. 2) or polycrystalline particles, and, also, different polytypes. This is related to the fact that in the condition of mass crystallization it is not possible to control the conditions of growth and the morphology of the individual crystals, and, therefore, there are many differences between the crystals grown simultaneously, related to the geometrical dimensions, the degree of perfection of the structure, and, also to the content of impurities.

Table 2. The growth conditions for $A^{IV}B^{VI}$ crystals from the gaseous phase.

Compound	Growth method	Temperature in the evaporation zone (K)	Temperature in the condensation Zone (K)	Duration of the growth (h)	Crystal shape	Crystal size (mm)	References
1	2	3	4	5	6	7	8
GeS	Static sublimation	$860 \div 880$	$770 \div 790$	$20 \div 24$	Plates, bands	Up to $20 \times 15 \times 0.2$	[358,363]
GeS : In	Static sublimation	$900 \div 910$	$810 \div 820$	$8 \div 10$	Needle	Length – $10 \div 30$, Thickness – $0.005 \div 0.01$	[41]
GeSe	Static sublimation	$970 \div 980$ 960	$810 \div 820$ 910	$20 \div 24$ 48	Plates, bands	Up to 20×15×0.2	[1] [37]]
GeSe	Static sublimation	gradient T $0.6 \div 2$ K/cm	$923 \div 928$		Plates	10×6×4	[4]
GeTe	Static sublimation	970	870		Prisms	Length of the boundaries up to 6 mm	[40]
SnS	Static sublimation	$1100 \div 1110$	$1010 \div 1020$	$20 \div 24$	Plates	Up to 8×6×0.2	[1]
SnSe	Static sublimation	$1100 \div 1110$	$1040 \div 1050$	$20 \div 24$	Plates	Up to 8×6×0.2	[1]
PbTe	Static sublimation	$1140 \div 1240$	$990 \div 1180$	$40 \div 70$	Rounded pieces	Weight up to 80 booles	[42]
2H –$SnSe_2$	Static sublimation	$1070 \div 1085$ 873	$950 \div 1020$ 773	$17 \div 20$ 500	Plates	Up to 10×10×0.1	[6, 11] [43]
SnSSe	Static sublimation	873	773		Plates	Up to 10×10×0.1	[43,59]
2H –$SnSe_2$	Static sublimation	$773 \div 1023$ 973	$773 \div 873$ 773	$50 \div 100$	Plates	10×10×0.1	[43]
β-GeS_2	Static sublimation	1073 943	873 813		Plates	6×6×0.4	[14]
β-$GeSe_2$	Static sublimation	$900 \div 970$	$850 \div 900$	$24 \div 36$	Plates	15×10×0.2	[4, 10]
β-$GeSe_2$	Static sublimation	973	873	24	Plates	10×10×0.1	[14]
$Si_2Te_3Si_2Te_3$	Static sublimation	1103	$1023 \div 1073$	$70 \div 80$	Plates	Thickness – 20, Diameter – 0.2	[17]
GeS_xSe_{1-x}	Static sublimation	$860 \div 880$	$760 \div 780$	24	Plates	20×15×0.2	[1, 48]

The dynamical version of the sublimation is achieved usually in large quartz tubes. Within the tube is placed in the corresponding temperature zone a small boat with the initial powder material. The transport of the vapors from the evaporation zone to the crystallization zone is carried out not only as a result of diffusion, as in

the case of statical method, but mainly with the help of the transporting gas, which passes along the quartz tube during all crystallization process. As transporting agents, usually are introduced inert gases (argon, helium and nitrogen).

The main shortcoming of the growth of layered mono-crystals of the type $A^{IV}B^{VI}$ and $A^{IV}B_2^{VI}$ using the sublimation method, consists in the fact that the size of the crystals is not large, as required by the industry. This is due to the low velocity of crystal growth from gaseous phase(ten – hundreds parts of millimeter per hour), difficulties of controlling the process of nuclei formation (especially for mass spontaneous crystallization) , complications in the stabilization of the growth conditions for long time, etc… Nevertheless, the advantage of this method is the possibility to control the process bellow the melting temperature (due to high vapor tension of the solid). Moreover, in the recrystallization process takes place a very efficient purification and, finally it is possible to obtain crystals without dislocations.

Method of chemical transport reactions. The method of crystallization with the participation of chemical reactions (method of chemical transport and decomposition or activation of the chemical compounds) was applied for the growth of crystals of materials with low value of the pressure of own vapors bellow the melting temperature or materials that loss essentially their stoichiometry during sublimation. The growth of crystals by chemical transport is achieved in closed systems; the decomposition method, or activation of the gaseous chemical compounds is conducted in flowing systems.

The advantage of the method of chemical transport reactions (CTR) over other methods of getting $A^{IV}B^{VI}$ and $A^{IV}B_2^{VI}$ from the gaseous phase is the possibility to achieve the growth to much lower temperatures. This allows for getting more perfect and stoichiometric crystals, and, also, gives the possibility to synthesize crystals of the low temperature modifications.

There exists two methods for the transportation of the gaseous phase in the chemical transport reactions: the current method and diffusion or convection method. By crystal growth in closed system (the quartz ampoule of 16÷20 cm in length and 2.0÷2.2 cm in diameter is sealed at both ends) it is used the natural hydrodynamic regime (diffusion and convection). As reagent carrier is used iodine. Because the growth velocity of the crystals decreases with the increase of pressure, then for enough productive crystallization process, it is not necessary a large amount of transporting agent. Usually in the ampoule is introduced iodine in an amount not higher than 1 mg/cm^3.

In the paper [49] it is studied in detail the mass transport in closed system $GeSe$-GeI_4 (quartz ampoule with diameter 15 mm and length 150 mm) with the temperatures in the region of evaporation and condensation of 793 and 693 K, The thermodynamic calculations of the partial pressure vapors GeSe, GeI_2, GeI_4, I, I_2, Se_n(n = 1 ÷ 8) have shown that in the conditions of the experiment the mass transport is achieved on the account of the interaction of solid GeSe with gaseous GeI_4 and the formation of gaseous GeI_2 and Se_2 with GeI_2 diffusion (chemical transport) and GeSe (sublimation) through gaseous phase. The above discussed facts can be expressed with the help of chemical reactions.

Considering that the disproportionation of the germanium di-iodide takes place according to the reaction:

$$Ge(solid) + GeI_4(gas) = 2GeI_2(gas) \quad (8)$$

The analogous reaction takes place in the transport of Ge and Sn chalcogenides. By considering the reaction (5.8) the transport of the Ge mono-chalcogenides in two-temperature furnace can be represented thus:

$$GeX(solid) + GeI_4(gas) \leftrightarrow 2GeI_2(gas) + ½ X_2 (gas) \quad 9)$$

In the high temperature domain the reaction takes place from left to right, and the gaseous products of the reaction diffuse in the low temperature region, where is activated the reverse reaction with the formation of the GeX mono-crystals.

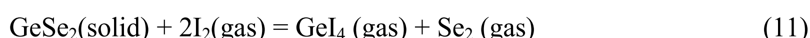
The results of mass-spectroscopy studies in the system $GeSe:GeI_4$ have shown that the reaction:

$$GeSe_2(solid) = GeSe(gas) +1/2\ Se (gas) \quad (10)$$

that decreases the concentration of Se_2(gas), which previously was neglected, has a high value, because sublimation-condensation of GeSe is the determining transport mechanism. For a general pressure of ~ 1 atm. the concentrations of other Ge-Se-I components of the vapor are co-measurable with the GeSe(gas) concentration.

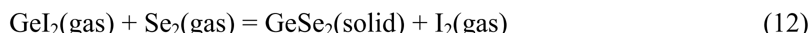
The study of the rate of GeSe transport in closed gas-transport system GeSe-GeI_4 for the temperature in the evaporation region 793 K and in the condensation region 693 K as a function of the pressure of inert gas in the range 0 -15 atm. has shown that for small pressures of the initial components, the process is developed in the diffusion domain, and with the increase of the pressure and the introduction of the inert gas, a significant role is played by the convection [49]. The thickness of the diffusion layer decreases with the increase of the pressure of the inert gas. After the results of the study of the morphology of the GeSe crystals as a function of growth conditions, it was established that in diffusion regime grow smooth platelets (010) with right boundary, and transition towards the diffusion-convective regime leads to the growth of dendrites with rough surface [45].

The transport of the germanium di-chalcogenides is best described by two separate reactions. In the domain of the source (hot region):



$$GeSe_2(solid) + 2I_2(gas) = GeI_4\,(gas) + Se_2\,(gas) \quad (11)$$

In the condensation domain (cold zone):



$$GeI_2(gas) + Se_2(gas) = GeSe_2(solid) + I_2(gas) \quad (12)$$

This means that GeI_4(gas) at high temperatures decomposes in GeI_2(gas) and I_2(gas). The iodine again participates in this process after the reaction (11).

The systematic study of the rate and mechanism of mass transport of SnS_2 for the use as transportation agents SnI_4 and elementary iodine, has been carried out in. The transport of SnS_2 has been performed in sealed quartz ampoules in horizontal two-zones furnace. The identification of the initial material as well as the products of transport has been carried out by X-ray diffraction. The amount of the source material was ~ 500 g, the quantity of the transporting agent changed from 0.01 mg to 1 g for SnI_4 and from 0.4 to 190 mg for iodine, the transportation time being 3 ÷115 h. There were determined the equilibrium partial pressures of the components of the gaseous phase for the temperature of the source and condensation, velocity of the transport as a function of the initial pressures of the transporting agent for different gradients of temperature: 648-723, 798-723, 923-823 K. In the first case, by using as transporting agent SnI_4, one observes both direct and indirect transport, and for higher temperatures, only direct transport. By using as transporting agent iodine, for the temperature gradient 648÷732 K the reverse transport has been observed for pressure of 0.3÷150 kPa.

With the help of thermodynamic calculations for these systems there were obtained the partial pressures of the main components of the gas: SnI_4, SnI_2, I_2, I, S_2, S_3, S_4, S_5, S_6, S_7 and S_8, and with these data have been written the basical transport reactions, that correspond with the observed general direction of the transport. On the basis of hypothetical pressure P* of SnS_2, determined as "solubility" of the SnS_2 in the gaseous phase, it has been introduced the parameter $\Delta P^* = P^*(SnS_2)T_1 - P^*(SnS_2)T_2$, where $T_2>T_1$. In the absence of the kinetic limitations for positive values ΔP* takes place the direct transport, and for negative values takes place the reverse transport. The presence of direct and reverse transport points to the existence of an inversion temperature for which the solubility of the solid phase is minimum.

On the example of crystallization of the layered SnS_2 compound by chemical transport reactions (CTR) method, it was shown the influence of the periodic oscillations of temperature in the condensation region on the growth process. The investigation of the dependence of the growth rate, size and rate of getting good crystals on the duration of experiments and on the period of temperature oscillation during growth has shown that in the process of growth of SnS_2 in the filled ampoule, with the CTR method, in the iodine vapors in the condensation zone, it is produced a periodical increase of temperature, and as a consequence, the dimensions of the grown crystals increase (up to 45 x 20 x 0.2 mm). In the presence of the temperature fluctuations takes place the preferential evaporation of not too large nuclei, which leads to the acceleration of the growth of large crystals on the account of small ones. For the determination of the duration of the heating and cooling cycles it is necessary to consider the thermal inertial effect of the furnace. The duration of every cycle must be enough high for producing an enough large growth of the crystals. The best results are obtained for high values of the

positive temperature oscillations, and the amplitude of the temperature oscillations must be as much as possible close to the used temperature gradient.

There were reported the experimental and theoretical data, of the investigations of the chemical gas transport in the system SnS_2-SnI_4, SnS_2-I_2, GeSe-GeI_4, GeSe-Xe, carried out on Earth and also in the micro-gravitation environment during the flights on Sky-Lab, Soyuz-Appolo and Shuttle, where the mass transport is limited by diffusion. In space conditions the morphology of the GeSe crystals is considerably improved during growth in the system GeSe-Xe, both by the method of chemical transport, and physical transport in vapors, which is essential for getting large crystals. On the orbital station have been obtained GeSe crystals of 1-2 orders of magnitude larger than the control samples, grown in the Earth conditions. Part of the crystals obtained in non-gravitational conditions, have had not contacts with the walls of the ampoules, and have shown mirror surfaces and high reflection [51, 52]. In the paper [53] the improvement of the quality of the crystals grown on Skylab is related to the absence of the convective component in the process of gas transport. The observation of high mass transport, compared with that waited in conditions of macro-gravity indicates, probably, another mechanism of mass transport in the system of reacting solid-gas phases. The convection, induced on Earth by gravitation has a negative influence on the crystal growth in the process of chemical transport reactions.

The growth conditions of the crystals SnTe and PbTe in the gas-transporting systems SnTe-Br_2 and PbTe-Br_2 have been studied in [55]. It was shown that the borders of the crystal are formed by the planes {111} and {100}, that exhibit step descent and anisotropy of the properties, in particular of the microhardness. The crystals exhibit high concentration of the free charge carriers and their structure is perfect. The method of chemical transport reaction is successfully used, for the growth of crystals of solid solutions $Ge_xPb_{1-x}Te$ and $Sn_2Pb_{1-x}Te$, too. Thus, in the paper [401] the process of growth has been achieved in two-zones vertical furnace in closed ampoules for pressure of $5x10^{-7}$ Torr with the use of oriented seed, fixed at the end of the ampoule. The crystal growth has been performed for a temperature gradient 1073 ÷ 1167 K along 35 days. As a result, grew crystals of homogeneous composition $Pb_xSn_{1-x}Te$, of up to 125 g weight, which have the dislocation density bellow 10^3 cm^{-2}.

In the Table 3 are given the optimal conditions of the growth process of the mono-crystals of IV-th group chalcogenides by the CTR method. The CTR method is most convenient for the growth of crystals of germanium and tin chalcogenides. The crystals obtained by this method are 5÷10 times thicker than the crystals obtained by sublimation.

Table 3 The growth conditions for $A^{IV}B^{VI}$ crystals in the method of CTR.

Compound	Reagent transporter	Temperature in the evaporation zone (K)	Temperature in the condensation zone (K)	Duration (h)	Crystal shape	Crystal size (mm)	References
1	2	3	4	5	6	7	8
GeSe	I_2	753	693		Planar needles, plates	10×1×0.01 8×8×0.5	[54]
GeSe	I_2(0.8÷1.7)	843	723		Plates	3 ÷ 7	[44]
GeSe	GeI_4	793	693		Plates	15×5×0.1	[44]
GeTe	I_2(1.0÷1.5)	863	713		Plates	4×6	[44]
SnS	I_2	920	820	24	Plates	8×5×0.1	[12]
SnTe	Br_2(1.4÷1.8)	1028 ÷ 1073	683 ÷ 743	5	Cube-like	Cube side 0.8 ÷ 1.2	[55]
GeS_2	I_2 (0.4)	950	840		Plates	Thickness up to 0.5	[18]
β-$GeSe_2$	I_2	800 ÷ 850	750 ÷ 800	24	Plates	10×7×0.2	[56]
GeS_2	I_2(0.9÷1.2)	823	673		Plates		[44]
SnS_2	I_2 (5)	1073 550 ÷ 800	973 500 ÷ 700	20 ÷ 200		4×4	[57] [43]
2H-SnS_2	I_2	960	870		Plates		[6]

		970 ÷ 1450	870 ÷ 1150				
18R-SnS_2	I_2	953	913		Plates		[58]
$SnSe_2$	I_2	973	873		Plates	10×1×0.1	[57]
2H-$SnSe_2$	I_2	863	843		Plates		[58]
$SnSe_2$	I_2	773	673		Plates	10×1×0.1	[59]
SnSSe	I_2	873	773		Plates	10×1×0.1	[43]
SnS_xSe_{1-x}	I_2	873	793	20	Plates	10×1×0.1	
$SiSe_2$	I_2	1080	1000		Needles	Length - 10 ÷ 15, Diameter – 0.1 ÷ 1	
$SnS_{2x}Se_{2(1-x)}$	I_2				Plates	10×1×0.1	
$Ge_xPb_{1-x}Te$	I_2	1167	1073	840		Weight up to 10 g	[61]
$Sn_xPb_{1-x}Te$	I_2	1163 ÷ 1053	883 ÷ 723		Octahedral needles		[62]

The main shortcomings of the method is the long duration of the process, preparation of crystals of small size and the introduction of the transporting agent in the lattice of the crystal. For the release of the transporting agent it is necessary to heat the crystal in vacuum.

The studies of the morphology of the crystals GeSe, $GeSe_2$ and GeTe, obtained by the CTR method, reported in [40, 44, 55], have shown that the habitus strongly depends on the feature of the transport. In the case of diffusion transport there are formed octahedral-type crystals, and in the case of convective transport are obtained platelet crystals. The ratio of the quantity of octahedral and platelet crystals decreases with the increase of the iodine pressure. The microscopic research of the surface of crystals have shown that the octahedral crystals (grown in the conditions of diffusion) have a more smooth surface, and the crystals of convective type have faces with high amount of disordered imperfect surfaces, as spirals, growth steps, and, also, dendrites.

The doping of the $A^{IV}B^{VI}$ crystals during growth by sublimation in vacuum or in gaseous environment (inert of chemically active) is achieved from solid sources when the doping impurity enters into the initial layer [9] or is mixed in a determined temperature zone of the furnace, which gives the necessary pressure of the impurity vapors for ensuring of the given level of crystal doping. The level of doping of the crystals with this method depends on the source temperature that makes the impurity doping, on the impurity concentration in the initial charge and the temperature of crystallization front. For getting homogeneous crystals these parameters must be maintained constants with high accuracy, because the vapor pressure of the impurity and their introduction in the crystalline lattice are exponential functions on the temperature of the source and crystal.

Method Pizzarello. In a row of cases one succeeds to get enough large AIVBVI mono-crystals from gaseous phase, by using to this aim a Bridgeman furnace with inverse temperature profile [13, 36, 63-67]. Firstly the method was used by Pizzarello [63] for the growth of bulk PbS crystals from the gas phase. The material that supports the recrystallization by the gaseous phase (sublimation-condensation or the reverse CTR) is mixed with the reaction agent - transporter in a quartz ampoule, whose upper part being drawn as a cone. In the cone one takes measures for ensuring the main growth of one from several spontaneous developments of crystallization nuclei. With this purpose the ampoule with the material is put in the furnace with temperature gradient, the cone is put firstly in the zone of the highest temperature (Fig. 4, b), and this cleans the internal surface of the ampoule on the account of transport of the main part of the crystalline nuclei, that are situated on the walls, e.g. as powders of the initial charge. In the next movement of the ampoule in the zone of highest temperatures, descends the bottom end of the ampoule (Fig. 4 c), and thus the cone is less heated. In the same time starts the process of sublimation-condensation or chemical transport from the precipitated material to the upper part of the ampoule. The narrow cone of the ampoule (length: 25÷40 mm) permits the crystal growth only from one of the appeared crystallization nuclei. The other crystalline particles vanish. If in the stage of the nuclei formation, the regime is correctly chosen and the crystallization process is carefully controlled, then all the initial charge can be transformed in an unique crystal.

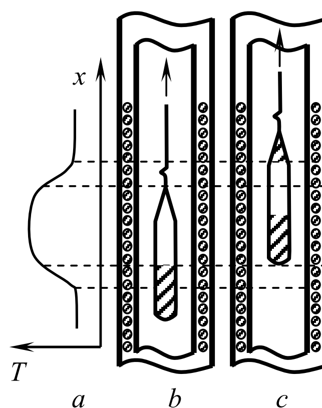


Fig. 4 The scheme for the GeS crystal growth by the method Pizzarello [36]:
a – profile of temperature along the vertical length of the furnace;
b. position of the ampoule with the material in the initial stages of drawing;
c. the stages of the crystal growth process.

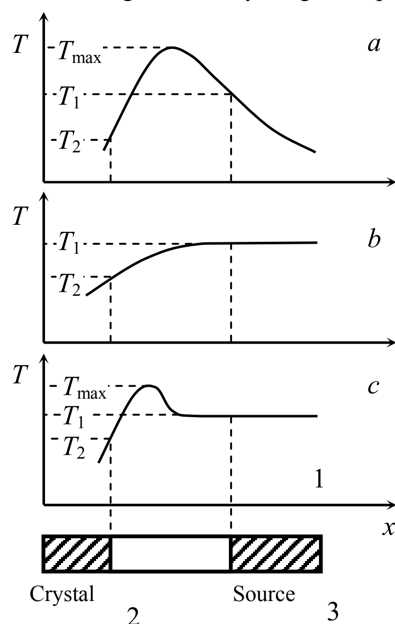


Fig. 5 The variants of the fixed distribution of the temperature [36].

Table 4 The conditions for crystal growth of $A^{IV}B^{VI}$ and $A^{IV}B_2^{VI}$ with the Pizzarello method.

Compound	Temp. profile	Temperat. bottom zone, K	Temp. upper zone, K	Sub-cooling temp., K	Drawing rate, mm/h	Crystal size (mm)	References
GeS	b,c	793 ÷ 853	With 40 K bellow T_{evap}	25	0.01 ÷ 0.2	20×40	[13, 36, 65]
GeSe	B	933	853	5 ÷ 20			[36]
GeSe		943	723	0.6 K/cm		Diameter - 10 ÷ 18	
GeTe	C	973	923	5 ÷ 30			[36]
SnS	A	1155	1113	10 ÷ 30			[36]
SnSe	C		1180	30 ÷ 50			[36]
SnSe	B	1073	1043	30		Diameter – 18	[679]
PbS	B		173	150			[63]
$GeSe_2$		953	873		4	6×3×0.3	[10]
Si_2Te_3		1173			0.01	Diameter - 20	[17]

For the growth of Ge and Sn mono-chalcogenide crystals, especially are used three variants of the fixed temperature distribution in the zones of growth of the furnace (Fig. 5) for source moving relative to the temperature profile [36]. The temperature profile (a) has a maximum between the source and the crystal, and on crystal the temperature is not constant. The temperature profile (b) is constant on the source and decreases monotonously from the temperature of the source down to the temperature of the surface layer of the crystal. The temperature profile (c) is a combination of the profile (a) and (b). It has a maximum between the source and crystal and is constant along the source.

The GeSe crystals have been grown with the Pizzarello method in quartz ampoules of diameter 20 mm and length 120 mm, evacuated down to the pressure of residual gases of 10^{-5} Torr [36-40]. The crystals have been grown in a vertical furnace with three temperature regions: 1 – for heating, 2- in the length of 5 cm, ensuring the temperature gradient of 25 K/cm, and the bottom part that determines the temperature of the evaporation of the source. The construction of the furnace allowed to conduct simultaneously growth of six crystals in six growth ampoules. High quality crystals have been obtained at the furnace temperature of 793-853 K, and the growth temperature was 40 K bellow the evaporation temperature. The ampoules have been moved in the upper region of the furnace with the speed not slower than 0.2 mm/h. The grown crystals show cleavage surfaces, parallel to the growth direction. The crystal density was 4.238 g/cm^3.

One-dimensional diffusion model for the growth of GeS crystal from gas phase in the closed ampoule, exhibiting conical form with transition to cylinder, is considered in the paper [66]. The source of the determined thickness is distributed in the depth of the cylinder. The crystal is seeded in the height of the cone and grows up to its complete formation. The problem is resolved in the hypothesis of the constant pressure in the ampoule. The viscosity of the gas and the gravitational stratification are neglected. It was shown that in this model the growth speed can be described with the relaxation time, which is the sum of two terms. One term is independent on the crystal length and describes the kinetics of the growth. The second term depends on the crystal length and describes the mass transport process. The calculations are supported by the experimental data for the growth of the GeS crystals in the ampoule with sharp ends.

5. Conclusions

In conclusion, we point out to one original method of getting mono-crystals of SnS_xSe_{1-x} solid solutions by thermo-conversion in iso-thermal conditions, proposed in [67]. The method consists essentially in the heating of the SnS mono-crystalline platelets in the presence of SnS+S and SnSe + Se powders at 973 K for 7 days. As a consequence of diffusion processes there were obtained crystals of solid solution of composition $SnS_{0.85}Se_{0.15}$ with the hole mobility of 88 cm^2/V.s.

References

[1] D. I. Bletskan, Phonon spectra and electron phenomena in ordered and disordered germanium chalcogenides (Ph. D. hab. Thesis) /russ./, Kiev, 1984, 447 pages.
[2] D. I. Bletskan, V. S. Gherasimenko, I. M. Migolinets, T. I. Shkoba, M. Iu. Sichka, Ukr. Fiz. J. **23**(3), 761 (1978).
[3] S. G. Karbanov, E. A. Statnova, V. P. Zlomanov, A. V. Novoselova, Study of the system Ge-Se near GeSe and the growth of crystals based on GeSe (russ.), Vestnik Mosk. Univ., Ser. Him. **13**(5), 531 (1972).
1147 (1976).
[4] D. I. Bletskan, V. S. Gherasimenko, M. Iu. Sichka, Three polymorphous of $GeSe_2$ crystals, Kristalografia, **24**(1), 83-89 (1979).
[5] D. I. Bletskan, V. A. Stefanovich, M. V. Potorii, Yu. V. Voroshilov, V. Iu. Slivka, Polymorphism of GeS_2, Kristalografia, **32**(2), 385-393 (1987).
[6] D. I. Bletskan, I. F. Kopinets, I. M. Migolinets, S. V. Mikularinets, Preparation and investigation of the properties of the single crystals of SnS_2, Izv. Akad. Nauk SSSR, Neorg. Mat. (russ.) **12**(12), 2128-2141 (1976).

[7] D. I. Bletskan, I. F. Kopinets, P. nP. Pogoretskii, E. M. Salkova, D. V. Chepur, Kristallografia, 20(5), 1008 (1975).
[8]D. I. Bletskan, V. I. Budianskii, I. F. Kopinets, S. V. Mikulaninets, Izv. Akad. Nauk SSSR, Neorg. Mat. 12(2), 202 (1976).
[9] D. I. Bletskan, N. V. Polajinets, M. M. Gsall, Izv. Akad. Nauk SSSR, Neorg. Mat. 25(10) 1623 (1989).
[10] D. I. Bletskan, N. V. Polajinets, M. V. Potorii, D. V. Chepur, Izv. Akad. Nauk SSSR, Neorg. Mat. 21(2) 214 (1985).
[11] D. I. Bletskan, Izv. Akad. Nauk SSSR, Neorg. Mat. 20(9) 1454 (1984).
[12] D. I. Bletskan, A. M. Evstigneev, I. F. Kopinets, I. M. Migolinets, V. A. Tiagai, Izv. Akad. Nauk SSSR, Neorg. Mat. 10(4), 735 (1974).
[13] D. I. Bletskan, I. I. Madiar, S. V. Mikulaninets, M. Yu. Sichka, Izv. Akad. Nauk SSSR, Neorg. Mat. 36(6) 663 (2000).
[14] S. A. Dembovskii, E. N. Loitsker, Izv. Akad. Nauk SSSR, Neorg. Mat. 3(11) 2092 (1967).
[15] J. Burgeat, G. Roux, A. Brenac, Sur une nouvelle forme crystalline de $GeSe_2$, J. Appl. Cryst. **8**(2), 325-327 (1975).
[16] Yu. Huang, J. Debram William, L. Fripp Archibal, J. Cryst. Growth. **104**(2), 315 (1990).
[17] K. Ploog, W. Stetter, A. Nowitzki, E. Schoenherr, Crystal growth and structure determination of silicon telluride Si_2Te_3, Mater. Res. Bull. **11**(8),
[18] N. P. Gavaleshko, A. I. Savchuk, P. P. Vatamaniuk, A. N. Liahovich, Izv. Akad. Nauk SSSR, Neorg. Mat. 17(3), 538 (1981).
[19] J. C. Mikkelsen, J. Cryst. Growth **49**(2), 253 (1980); J. C. Mikkelsen, Rev. Sci. Instrum. **51**(11), 1564 (1980).
[20] I. Lefkowitz, M. Shields, G. Dolling, J. Cryst. Growth **6**(2), 143 (1970).
[21] A. R. Calawa, T. C. Hatman, M. Finn, P. Youtz, Trans Metallurg. Soc. AIME **242**(3), 374 (1968).
[22] K. L. I. Kobayashi, Y. Kato, K. F. Komatsubara, Progr. Cryst. Growth and Charact. **1**(2), 117 (1978).
[23] N. P. Gavaleshko, M. V. Kurik, A. I. Savchuk, Fiz. I Tehn. Poluprovod. 1(7), 1099 (1967).
[24] G. Busch, C. Fröhlich, F. Hulliger, E. Steigmeier, Struktur, elektrische und thermoelektrische Eigenschaften von $SnSe_2$, Helv. Phys. Acta **34**(4), 359-368 (1961).
[25] R. H. Akchurin, V. N. Vigdorovici, A. A. Lobanov, V. V. Marichev, V. B. Ufimtsev, Izv. Akad. Nauk SSSR, Neorg. Mat. 12(5) 838 (1976).
[26] D. I. Bletskan, V. P. Terban, M. I. Gurzan, M. V. Potorii, Preparation, structure and photoelectric properties of $PbGeS_3$ and Pb_2GeS_4 crystals, Izv. Akad. Nauk SSSR, Neorg. Mat. **26**(3) 509-514 (1990).
[27] D. I. Bletskan, E. Yu. Petresh, V. A. Redko, Ukr. Fiz. Zhurn. 27(12) 1890 (1983).
[28] R. J. Baughman, R. A. Lefever, Mat. Res. Bull. **4**(10), 721 (1969).
[29] P. F. Weller, J. Electrochem. Soc. **113**(1), 90 (1966).
[30] M. Bensoussan, A. Brenac, J. Thomas J. Cryst. Growth **15**(1), 79 (1972).
[31] L. E. Shelimova, Z. U. Djabua, N. H. Abrikosov, Izv. Akad. Nauk SSSR, Neorg. Mat. 9(7) 1254 (1973).
[32] S. E. R Hiscocks, J. Mater. Sci. **4**(), 310 (1969).
[33] V. F. Mihailov, O. V. Pelevin, E. B. Sokolov, A. M. Sokolov, Collection of scientific papers on microelectronics (russ.) Moscow, Inst. Electron-technique, Iss. 24, p. 38 (1976).
[34] E. P. A. Metz, R. C. Miller, R. Mazelsky, J. Appl. Phys. **33**(6), 2016 (1962).
[35] E. A. Irene, Z. Aanorg. Allg. Chem. **411**(2), 182 (1975).
[36] E. Schönherr, Growt and Properties, Springer, Berlin, p. 51, 1980.
[37] D. S. Kyriakos, T. K. Karkostas, N. A. Economou, J. Cryst. Growth

35, 223 (1976).
[38] E. Schönherr, J. Cryst. Growth. **44**(5), 604 (1978).
[39] D. I. Bletskan, I. F. kopinets, I. M. Migolinets, S. V. Mikulaninets, I. D. Rubish, M. Yu. Sichka, Popluprovod. Tehn. i Mikroelektron., Kiev, Naukovaia Dumka, Iss. 25, p. 3117 (1977).
[40] N. N. Koreni, L. I. Postnova, Izv. Akad. Nauk SSSR, Neorg. Mat.15(12) 2106 (1979).
[41] D. I. Bletskan, R. Yu. Indus, Izv. Akad. Nauk SSSR, Neorg. Mat. 18(4) 544 (1982). B **29** (12), 6732 (1984).
[42] L. A. Klinkova, V. K. Gartman, L. P. Guldiava, S. A. Zverikov, Izv. Akad. Nauk SSSR, Neorg. Mat. 23(7) 1132 (1987).
[43] F. Lévy, Nuovo Cimento **B38**(2), 359 (1977).
[44] H. Wiedemeier, E. A. Irene, A. K. Chaudhuri, J. Cryst. Growt. **13/14**(1), 393 (1972).
[45] H. Wiedemeier, E. A. Irene, Z. anorg. Allg. Chem. **400**(1), 59 (1973)
[46] M. Rubinstein, G. Roland, A monoclinic modification of germanium disulfide, GeS_2, Acta Crystallogr. B, **27**(2), 505-506 (1971).
[47] I. Hatta, K. L. I. Kobayashi, A mean-field behavior of the specific heat at the phase transition of SnTe with a low carrier concentration, Solid State Commun., **22**(12), 775-777 (1977).
[48] D. I. Bletskan, V. S. Gherasimenko, I. M. Migolinets, M. Yu Sichka, T. I. Shkoba, The formation of the solid solutions in the system GeS-GeSe and their physical properties, Ukr. Fiz. Y. **21**(10), 158-1590 (1976).
[49] H. Wiedemeier, D. Chandra, F. C. Klaessig, J. Cryst. Growth. **51**(2), 345 (1980).
May, 12-17, 1985, Pennington, 1985, p. 38.
[50] F. A. S. Al-Alamy, A. A. Balchin, J. Cryst. Growth **39**(2), 275 (1977).
[51] H. Wiedemeier, S. B. Trivedi, X. R. Zhong, R. C. Whiteside, J. Electrochem. Soc. **133**(5), 1015 (1986).
[52] H. Wiedemeier, S. B. Trivedi, Naturwissenscaften. **73**(7), 375 (1986).
[53] H. Wiedemeier, F. Klaessig, E. A. Irene, J. Cryst. Growth **31**, 36 (1975).
[54] J. G. a. M. Van den Dries, R. M. A. Lieth, Phys. Status. Solidi (a), **5**(3), K1741 (1971).
[55] S. S. Varshava, S. N. Bekesha, I. V. Kurilo, L. N. Pelekh, Izv. Akad. Nauk SSSR, Neorg. Mat. 23(8), 1286 (1987).
[56] J. Burgeat, G. Roux, A. Brenac, Sur une nouvelle forme crystalline de $GeSe_2$, J. Appl. Cryst. **8**(2), 325-327 (1975).
[57] D. L. Greenaway, R. Nitsche, J. phys, Chem. Solids. **26**(9), 1445 (1965).
[58] J. Burgeat, G. Roux, A. Brenac, Sur une nouvelle forme crystalline de $GeSe_2$, J. Appl. Cryst. **8**(2), 325-327 (1975).
[59] R. Nakata, M. Yamaguchi, S. Zemautsu, M. Sumita, J. Phys. Soc. Japan **32**, 1153 (1972).
[60] E. A. Hauschild, C. R. Kannewurf, J. Phys. Chem. Solids, **30**(2), 353 (1969).
[61] S. C. Parker, J. E. Pinnell, R. E. Jhonson, J. Electron. Mater. **3**(4), 731 (1974).
SSSR, Neorg. Mat. 2(3), 546 (1975).
[62] L. I. Bezrodnaia, N. I. Makarova, E. P. Strukova, Yu. S. Harionovskii, S. G. Yudin, Rost Kristalov, M. Nauka, T. 9, 1972, p. 231.
[63] F. Pizzarelo, J. Appl. Phys. **25**(6), 804 (1954).
[64] E. Schönherr, W. Stetter, J. Cryst. Growth. **30**(1), 96 (1975).
[65] E. Hartmann, E. Schönherr, J. Cryst. Growth. **51**(1), 140 (1981).
[66] R. Lauck, E. Schönherr, J. Cryst. Growth, **66**(1), 121 (1984).
[67] W. Albers, J. Verberkt, Philips Res. Repts. **25**(1), 17 (1970).