

**FORMATION, CRYSTALLOGRAPHIC CLASSIFICATION AND
PROPERTIES OF COMPOUNDS IN A^I - B^{III} - C^{VI} SYSTEMS**

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Formation, Crystallographic Classification and Properties of Compounds in $A^I - B^{III} - C^{VI}$ Systems

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Abstract

The complex compounds in the $A^I - B^{III} - C^{VI}$ systems (A^I - Li, Na, K, Rb, Cs, Ag, Cu; B^{III} - Ga, In, Tl; and C^{VI} - S, Se, Te) are promising semiconductor, electro-optic, nonlinear-optic, luminescence, pyroelectric, and piezoelectric materials. Especially, compounds of the $A^I B^{III} C_2^{VI}$ - type can be used for practical applications. Many of these have not been synthesized and investigated yet, which is related, to a significant extent, to technical difficulties in producing these compounds. Therefore, this work was dedicated to overview the research of the ternary compounds in the $A^I - B^{III} - C^{VI}$ systems including syntheses, single crystal growth, phase equilibrium, properties; theories of formations of the complex compounds, crystallographic classification, and changing properties; and predicting the possibility of the existence of the new compounds and their crystal structure and properties. The analysis of the ionic-radii ratios and the crystal structural types of the compounds shows that the variation in the crystal structure of the $A^I B^{III} C_2^{VI}$ type compounds in the systems $A^I - B^{III} - C^{VI}$ directly depends upon the magnitude of the ionic-radii ratio of alkaline metal (A^I) to chalcogen (C^{VI}). The crystal structures of the $A^I B^{III} C_2^{VI}$ type of compounds can be classified into three crystal structural types: ZnS, NaCl, and TiSe. The developed theory allows performing the prediction of crystal structures of non-investigated $A^I B^{III} C_2^{VI}$ compounds. It was discovered that the density, melting point, and width of the band gap directly depend upon the sum of the atomic numbers of the elements (ΣZ) for compounds of the same type of crystal structure, which allows predicting some properties for non-investigated compounds. The decrease in the melting point and the band gap widths (E) of the compounds with increasing ΣZ indicates weakening of their stability as the metallic component of the chemical bonding increases.

Introduction

The complex compounds in the $A^I - B^{III} - C^{VI}$ systems are known to be promising materials for advanced technology, where A^I - Li, Na, K, Rb, Cs, Cu, Ag; B^{III} - Ga, In, Tl; C^{VI} - S, Se, Te. The ternary compounds provide a number of benefits in comparison with single elements and binary compounds. Especially, compounds of the $A^I B^{III} C_2^{VI}$ - type are known to be promising semiconductor, electrooptic, and nonlinear-optical materials [1,2]. Many of these, especially compounds contain alkali metals, have not been investigated yet and those, that have been synthesized, have been studied inadequately, which is related, to a significant extent, to technical difficulties in producing compounds of the $A^I B^{III} C_2^{VI}$ - type in the individual state. Prepared samples of these compounds by exchange reactions contain 2 wt. % of oxygen [3]. Synthesis from the components is difficult due to the high chemical reactivity of the alkali metals.

The goal of this work is to review the research of the complex compounds in the $A^I - B^{III} - C^{VI}$ systems (A^I - Li, Na, K, Rb, Cs, Cu, Ag; B^{III} - Ga, In, Tl; C^{VI} - S, Se, Te) by means of synthesizing compounds, growing single crystals, investigating their properties and phase equilibrium, developing the theories of formations of the complex compounds, establishing the rules governing their crystallographic classification and properties, and predicting the possibility of the existence of the new compounds and their crystal structure and properties.

Results and Discussions

The possibility of forming ternary compounds in the $A^I - B^{III} - C^{VI}$ systems has been considered from the viewpoint of the physico-chemical criterion of the formation of compounds [4, 5]. In accordance with this approach, an analysis of the nature of the physico-chemical interactions in the $A^I - C^{VI}$ and $B^{III} - C^{VI}$ binary systems, which compose the ternaries, has been carried out. The physico-chemical interactions are determined as interactions between the particles of the material system by the substance and energy at corresponding conditions. Afterwards, the possibility of forming ternary compounds has been evaluated, considering the physical-chemical interactions in the basic binary systems and such factors as the electronic structure, polarization potential, ionic- and covalent-radii, thermodynamic stability, crystal structure, which influence on the type of the forming chemical bonds. The combination of the physical-chemical criterion of formation of ternary compounds with the character of chemical bonding between particles (atoms, ions, molecules, etc.) in the initial binary and in the forming ternary compounds can be used to optimize the prediction of the existence of new phases and their properties.

It has been found that the ternary compounds in the $A^I - B^{III} - C^{VI}$ systems exist on the $A_2^I C^{VI}$ - $B_2^{III} C_3^{VI}$, $A_2^I C^{VI} - B_2^{III} C^{VI}$, and $A^I C^{VI} - B_2^{III} C_3^{VI}$ sections. From the position of the physical-chemical criterion of formation of compounds, the existence of new compounds is predicted in the $A^I B^{III} - A_2^I C^{VI}$, $A^I B^{III} - B_2^{III} C^{VI}$, $A^I B^{III} - C^{VI}$, and $A^I B^{III} C^{VI} - B^{III} C^{VI}$ systems (Fig. 1) [6-8].

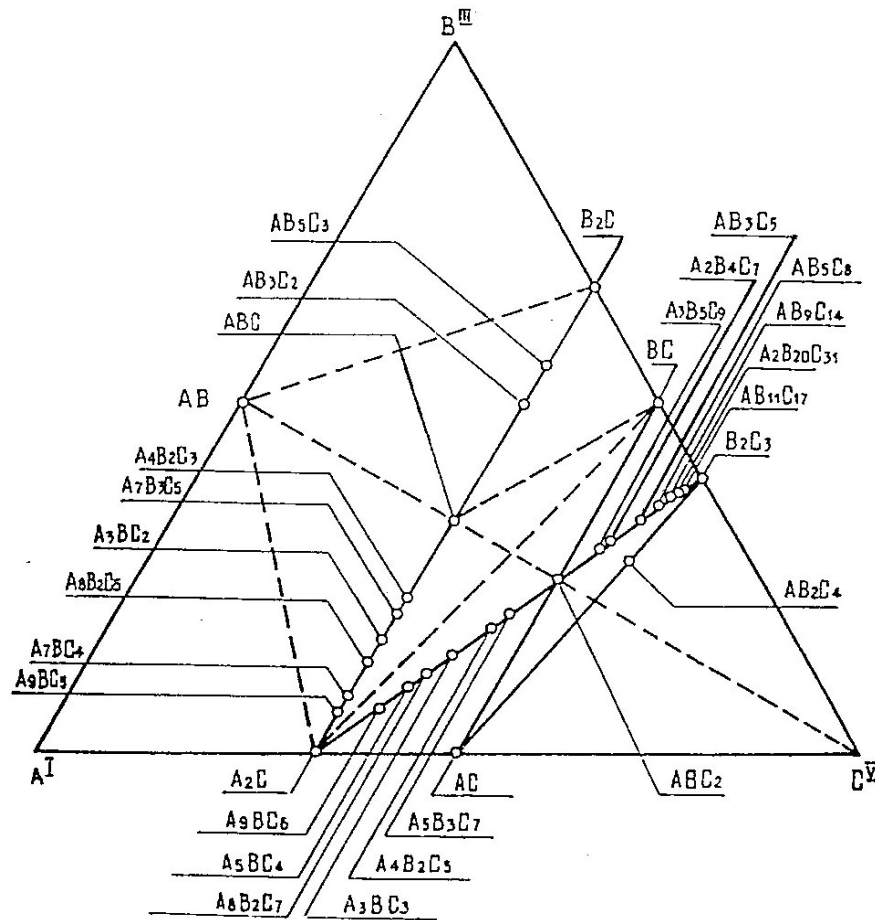


Fig. 1. The formation of the ternary compounds in the $A^I - B^{III} - C^{VI}$ systems. (The pseudobinary systems not studied are marked by dotted line).

The differences of the character of the physical-chemical interactions in the $A^I - B^{III} - C^{VI}$ are connected with the peculiarities of the electronic structure of atoms, which cause the nature of chemical bonds in compounds.

The comparison of the physical-chemical interactions in the $A^I - B^{III} - C^{VI}$ systems shows that the most stable chemical compounds are $A^I B^{III} C_2^{VI}$ - type, which form on the $A_2^I C^{VI} - B_2^{III} C_3^{VI}$ quasibinary section. The investigated $A_2^I C^{VI} - B_2^{III} C_3^{VI}$ systems (by us) represented in Fig. 2 [9-11].

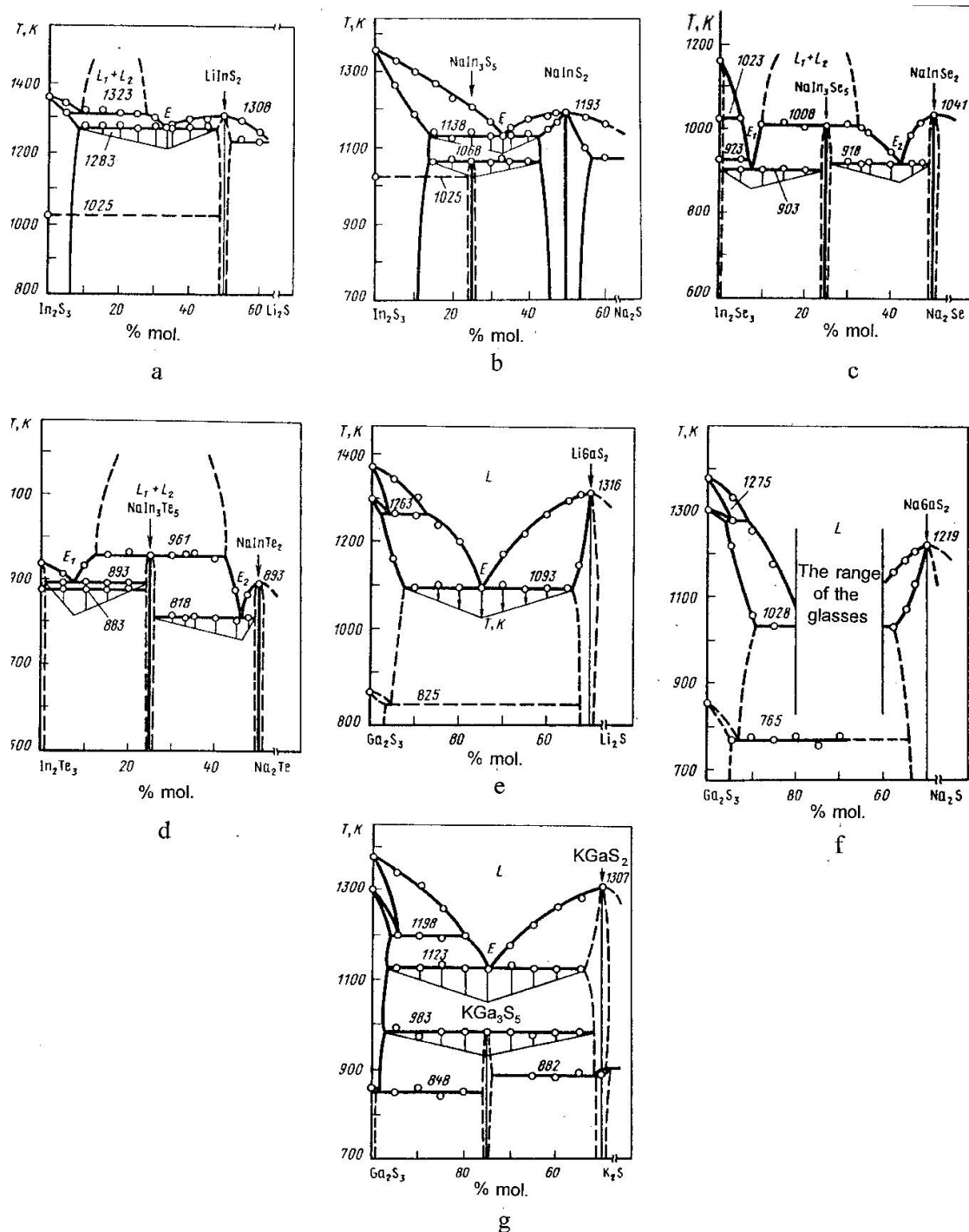


Fig. 2. The diagrams of the $A_2^I C^{VI} - B_2^{III} C_3^{VI}$ pseudobinary systems. (a. $Li_2S - In_2S_3$; b. $Na_2S - In_2S_3$; c. $Na_2Se - In_2Se_3$; d. $Na_2Te - In_2Te_3$; e. $Li_2S - Ga_2S_3$; f. $Na_2S - Ga_2S_3$; g. $K_2S - Ga_2S_3$).

The peculiarity of the synthesis and the single crystal growth of the $A^I B^{III} C_2^{VI}$ - type compounds has been determined by differential approach to the concerning substances containing alkali metals, on the one side, and copper and silver, on the other side, and the phase equilibrium in the corresponding systems, and a number of technological factors, such as matter and form of the reaction containers, temperature, pressure, temperature gradients, rate of crystallization, oriented crystal seed in the process of growth, etc. With the consideration of the safe and reproduction way, the compounds $A^I B^{III} C_2^{VI}$, containing alkali metal, were synthesized by melting together the corresponding alkali metal, $B_2^{III} C_3^{VI}$ and chalcogen in the inert atmosphere in order to avoid interaction of alkali metal with air. The compounds, containing copper and silver, were synthesized by reaction between corresponding $A_2^I C^{VI}$ and $B_2^{III} C_3^{VI}$. Such methods of syntheses enable us to prepare compounds of the stoichiometric composition and also to exclude the tendency towards explosion during the synthesis process. Considering the constructed phase diagrams of the corresponding systems, the single crystals have been grown by directed crystallization of the melts using the Bridgman–Stockbarger method [6, 12-15]. The samples of single crystals are presented in Fig. 3.

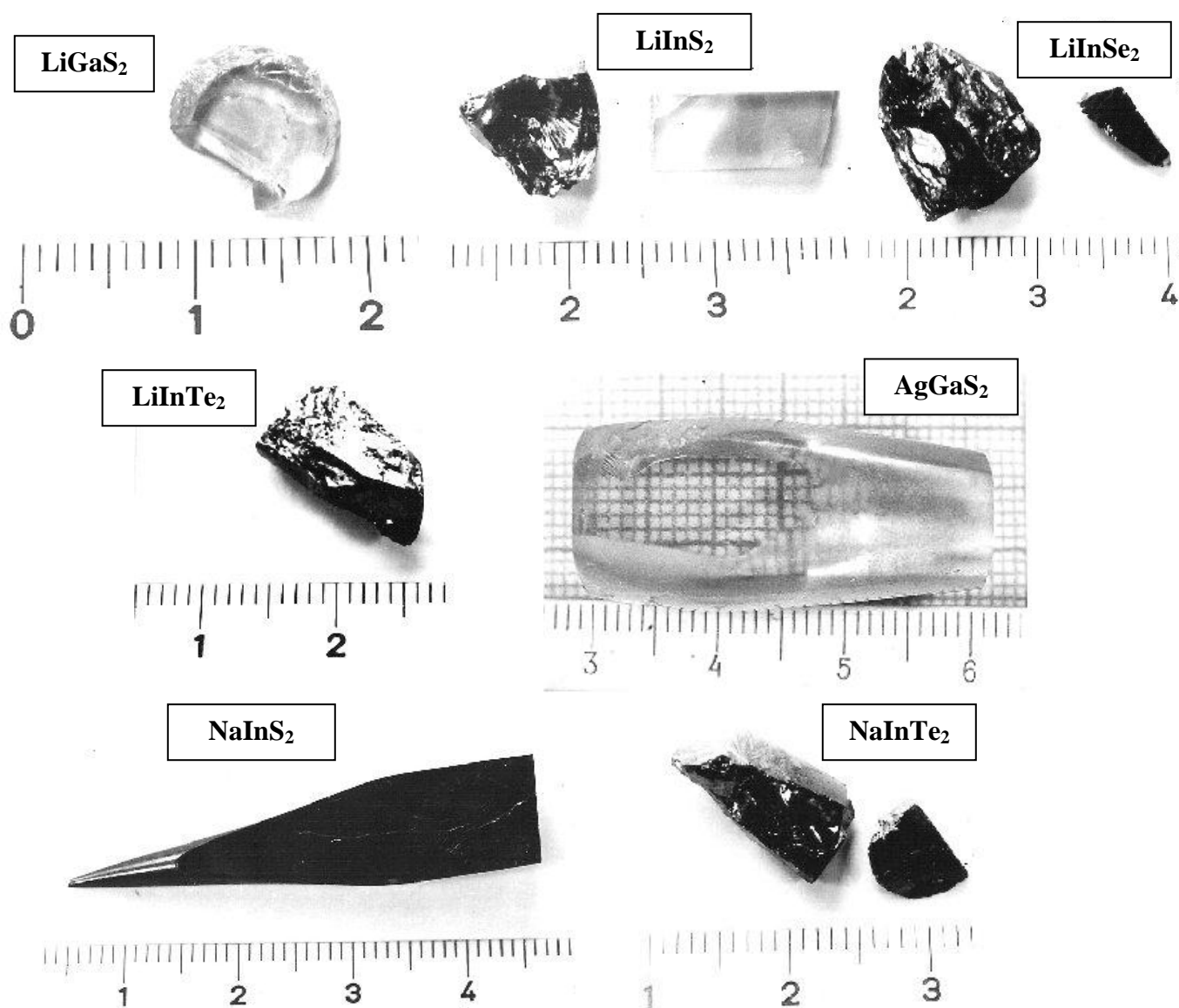


Fig. 3. The single crystals of the $A^I B^{III} C_2^{VI}$ compounds

The crystal structure and other physical and chemical properties of the $A^I B^{III} C_2^{VI}$ - type compounds have been investigated [6-16]. The obtained data have been analyzed to find governing rules for their properties. The crystallographic data for the $A^I B^{III} C_2^{VI}$ - type compounds are presented in Table 1. In spite of being the same type of compound, they have different structures, which are caused by the different types of chemical bonding between the atoms and the corresponding differences in the atomic coordination.

Table 1.

Crystallographic Data on the $A^I B^{III} C_2^{VI}$ - Type Compounds

Compounds	Spase Group or Crystal Sysytem	Unit Cell Parameters				Number of formula units, Z	References
		a nm	b nm	c nm	Angles deg.		
Compounds with the structure produced from ZnS							
LiGaS ₂	<i>Pna2₁</i>	0.651	0.786	0.622		4	[20]
LiInS ₂	<i>Pna2₁</i>	0.6887	0.8050	0.6474		4	[14]
LiInSe ₂	<i>Pna2₁</i>	0.7218	0.8441	0.6772		4	[21]
Compounds with the structure produced from NaCl							
NaInS ₂	$\bar{R}3m$	0.3838		1.989		3	[22]
NaInSe ₂	$\bar{R}3m$	0.3972		2.089		3	[22]
Compounds with the structure produced from TlSe							
NaGaTe ₂	14/mcm	0.822		0.688		4	[23]
NaInTe ₂	14/mcm	0.833		0.727		4	[24]
KInTe ₂	14/mcm	0.852		0.739		4	[24]
KGaSe ₂	Triclinic	0.766	0.766	6.040	$\alpha = \beta = \gamma \approx 90$	32	[23]
KInSe ₂	Triclinic	0.803	0.803	6.128	$\alpha = \beta = \gamma \approx 90$	32	[23]
KGaTe ₂	Triclinic	0.834	0.834	6.940	$\alpha = \beta = \gamma \approx 90$	32	[23]
KInS ₂	Monoclinic	1.564	1.088	1.116	$\beta = 103$	16	[17]
KTlS ₂	Monoclinic	1.586	1.116	1.112	$\beta = 102$	16	[17]
RbInS ₂	Monoclinic	1.564	1.110	1.109	$\beta = 100$	16	[17]
CsInS ₂	Monoclinic	1.608	1.114	1.131	$\beta = 101$	16	[17]
RbTlS ₂	Monoclinic	1.589	1.107	1.130	$\beta = 101$	16	[17]
CsTlS ₂	Monoclinic	1.599	1.132	1.138	$\beta = 100$	16	[17]
CsGaS ₂	C2/c	0.7425	1.2210	0.5907	$\beta = 113.1$	4	[25]

The experimental values of the $A^I - C^{VI}$ and $B^{III} - C^{VI}$ interatomic distances were compared with the sum of the covalent and ionic radii to analyze the type of chemical bonding in the $A^I B^{III} C_2^{VI}$ - type compounds. The ionic radius values were taken from [18], whereas the Pauling covalent radii were taken from [19]. The limited experimental data on the $A^I - C^{VI}$ and $B^{III} - C^{VI}$ interatomic distances, obtained from X-ray crystal structural investigations, and the sum of the corresponding ionic and covalent radii are presented in Table 2.

Table 2.

Experimentally Observed and Calculated Interatomic Distances for $A^I B^{III} C_2^{VI}$ - type Compounds

Compounds	Interatomic distances of $A^I - C^{VI}$, nm	Sum of ionic radii of A^I & C^{VI} , nm [18]	Sum of covalent radii of A^I & C^{VI} , nm [19]	Coordination number of A^I	Interatomic distances of $B^{III} - C^{VI}$, nm	Sum of ionic radii of B^{III} & C^{VI} , nm [18]	Sum of covalent radii of B^{III} & C^{VI} , nm [19]	Coordination number of B^{III}	References for interatomic distances
LiInS ₂	0.237-0.250	0.250	0.227	4	0.244-0.246	0.274	0.248	4	[14]
NaInS ₂	0.287	0.289	0.261	6	0.263	0.274	0.248	6	[22]
NaInSe ₂	0.300	0.291	0.274	6	0.276	0.285	0.261	6	[22]
NaGaTe ₂	0.349	0.309	0.294	8	0.265	0.273	0.264	4	[23]
NaInTe ₂	0.356	0.309	0.294	8	0.279	0.303	0.281	4	[24]
KInTe ₂	0.364	0.344	0.340	8	0.282	0.303	0.281	4	[24]
CsGaS ₂	0.364-0.372	0.347	0.339	8	0.227-0.228	0.244	0.231	4	[25]

From Table 2, it can be seen that the fractions of the ionic and covalent components of the chemical bonds between the atoms depend upon the composition of the compound. The $B^{III} - C^{VI}$ bonds are predominantly covalent and tetrahedral coordination of the chalcogen occurs for B^{III} . As a consequence, tetrahedral units of $B^{III} C_4^{VI}$ are formed in the crystal structure of the $A^I B^{III} C_2^{VI}$ - type compounds. The compounds NaInS₂ and NaInSe₂ are exceptions since their structure is NaCl-based; the $B^{III} - C^{VI}$ bonds have predominantly an ionic character, forming $B^{III} C_6^{VI}$ octahedral. The coordination number (C.N.) of B^{III} is equal to 6. The $A^I - C^{VI}$ bonds have primarily an ionic character, if A^I are alkali metals. X-ray structural data about the nature of the $A^I - C^{VI}$ and $B^{III} - C^{VI}$ chemical bonds agree with the differences between the electro-negativities of the respective components [26].

Therefore, the $B^{III} - C^{VI}$ and Cu (Ag) - C^{VI} bonds are predominantly covalent and $A^I - C^{VI}$ bonds (A^I - alkali metals) - ionic [6, 16]. It should be mentioned that Tl - C^{VI} bonds, on the one side, are primarily ionic, if the oxidation number is equal to +1, and on the other side, are covalent, if the oxidation number is +3. There is limited information contained in the literature about the preparation and structure of compounds of this type with thallium (III) only, viz., KTlS₂, RbTlS₂, and CsTlS₂ [17]. The physico-chemical interaction in the $A^I - B^{III} - C^{VI}$ is different, when B^{III} is Tl, because the structure of the outer-electron shells of thallium differs from those of gallium and indium because of the presence of 5*d* and 4*f* sublevels, the energy values of which are above the 6*s* energy levels. The corresponding screening 'makes the 6*p*-electrons of thallium the primary participants in the formation

of the chemical bond. The metallic component of the chemical bonding increases by replacing $S \rightarrow Se \rightarrow Te$. As a consequence, the above compounds can be characterized as the compounds with a mixed covalent-ionic-metallic type bonds, depending on the composition of the elements.

The analysis of the ionic-radii ratios and the crystal structural types of the compounds shows that the variation in the crystal structure of the $A^I B^{III} C_2^{VI}$ type compounds, in the systems of $A^I - B^{III} - C^{VI}$, directly depends upon the magnitude of the ionic-radii ratio of alkaline metal (A^I) to chalcogen (C^{VI}), $R_{A^+}/R_{C^{2-}}$. With increasing $R_{A^+}/R_{C^{2-}}$ ratio (it is marked as D), the coordination number (C.N.) of alkali metal (A^I) increases and the crystal structure of the corresponding $A^I B^{III} C_2^{VI}$ ternary compound changes accordingly. This established rule allows us to predict the crystal structure of compounds, which have not yet been investigated. The $A^I B^{III} C_2^{VI}$ compounds can be classified into three crystal structure types based on the crystallographic data (Table 2). The crystal structures of the $A^I B^{III} C_2^{VI}$ type of compounds can be classified into three crystal structural types, derivatives from ZnS -, NaCl -, and TlSe – crystal structural types [6, 16]. The crystal structures of these compounds are presented on Figure 4.

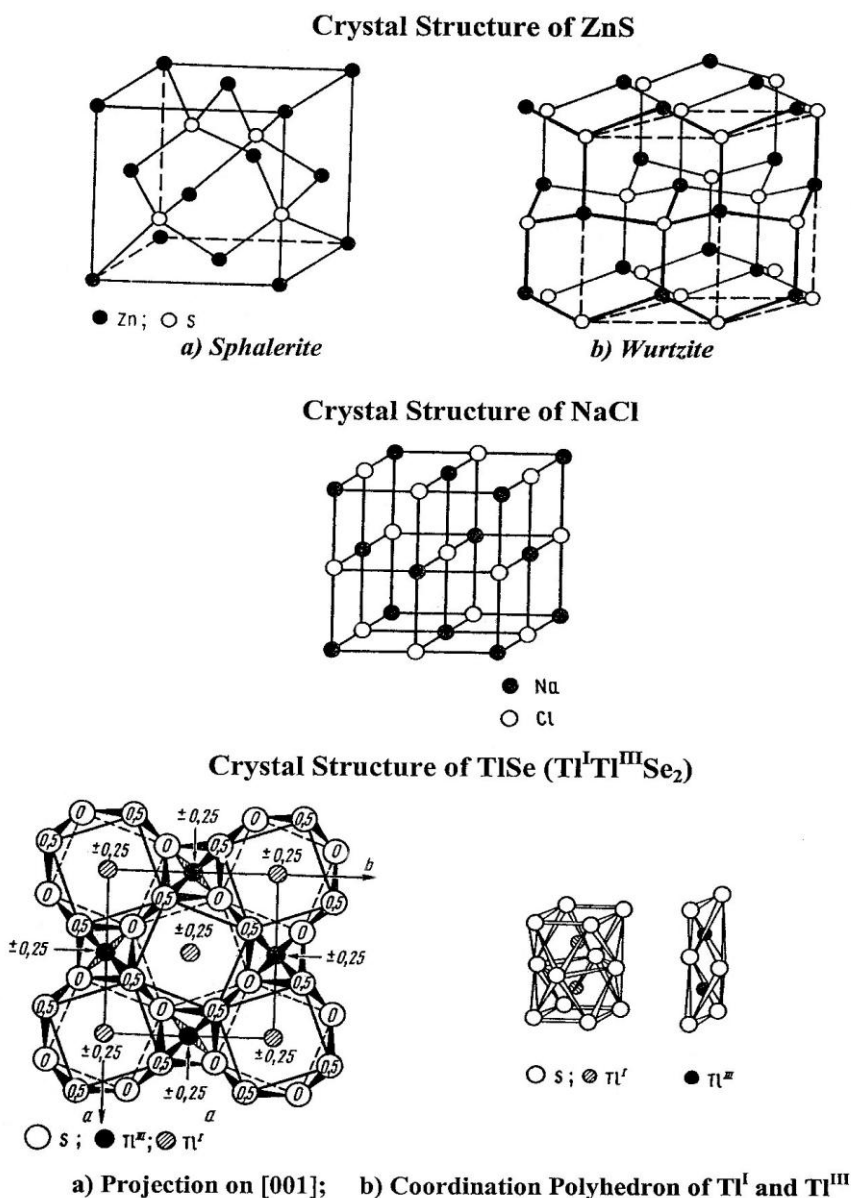
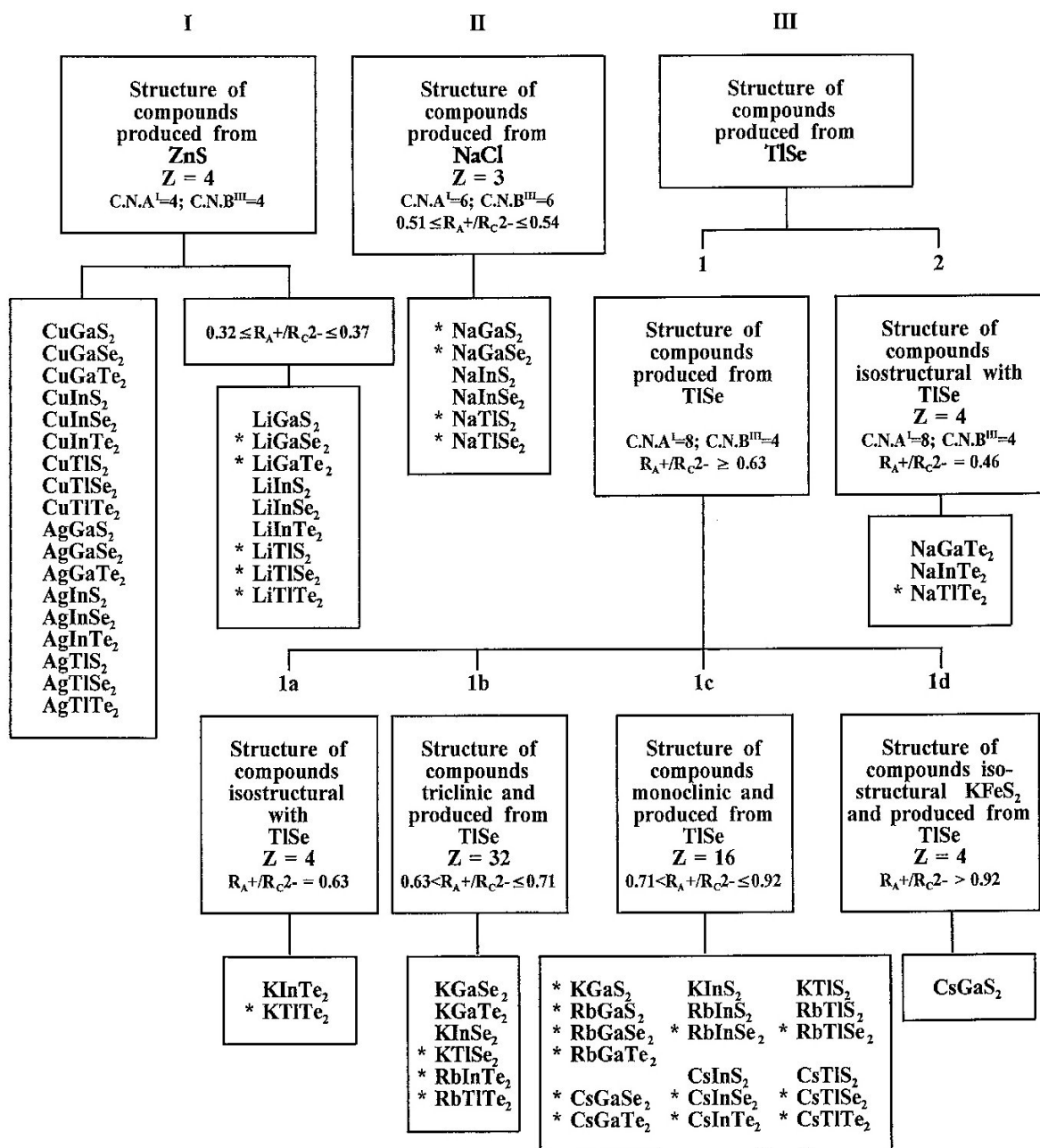


Figure 4. The crystal structures of the ZnS, NaCl, and TlSe compounds.

The crystallographic classification of the $A^I B^III C_2^{VI}$ type compounds is presented in Table 3 [6, 16].

Table 3.

THE CRYSTALLOGRAPHIC CLASSIFICATION OF THE $A^I B^III C_2^{VI}$ -
TYPE COMPOUNDS.



* - The asterisk indicates the compounds have not been investigated yet.

Z - The number of formula units.

C.N. - The coordination number.

According to this crystallographic classification the copper, silver and lithium ternary compounds have crystal structures derivative from ZnS, tetrahedral atomic coordination (C.N. of A^I and $B^{III} = 4$), and the magnitude of the ionic-radii ratios of D vary in the range 0.32 - 0.37 for lithium compounds. The basic structural units are the $A^I C_4^{VI}$ and $B^{III} C_4^{VI}$ tetrahedral (Fig. 4). In the crystal structure, metallic atoms fill half of the tetrahedral vacancies in an ordered arrangement in dense packing of the chalcogen atoms. The above compounds belong to the type-**I** structure (Table 3).

The value of D is 0.51-0.54 for $NaInS_2$ and $NaInSe_2$. They have crystal structures derivative from NaCl and isostructural with α - $NaFeO_2$. Layers of A^I and B^{III} atoms alternately divide the C^{VI} layers in such a manner that both types of cations are octahedrally surrounded by the chalcogenide ions with an ordered arrangement (C.N. of A^I and $B^{III} = 6$) (Fig. 4). The compounds belong to the structural type-**II** (Table 3).

According to the crystallographic data (Table 1), the compounds $NaGaTe_2$, $NaInTe_2$, $KInTe_2$, $KGaSe_2$, $KInSe_2$, $KGaTe_2$, $KInS_2$, $KTIS_2$, $RbInS_2$, $CsInS_2$, $RbTIS_2$, $CsTIS_2$, and $CsGaS_2$ crystallize in a structure derivative from TlSe (Fig. 4). They belong to the structural type-**III** (Table 3).

The compound TlSe must be considered as $Tl^I Tl^{III} Se_2$ since thallium atoms occupy two different crystallographic positions in the crystal structure [28]. It can be considered that the oxidation number for Tl^I is equal to +1 and for Tl^{III} is equal to +3 correspondingly. The Tl^I atoms are arranged in the centers of cubes, which are slightly deformed and twisted by a very small angle, with selenium atoms at the vertices (C.N. of $Tl^I = 8$), and Tl^{III} atoms are arranged at the centers of the tetrahedral (C.N. of $Tl^{III} = 4$) and form chains with surrounding selenium atoms (Fig. 4). Accordingly, in the structure of the above compounds of the $A^I B^{III} C_2^{VI}$ -type, the A^I atoms are arranged at the Tl^I sites but the B^{III} atoms are at the Tl^{III} sites, due to which the C.N. of $A^I = 8$ but the C.N. of $B^{III} = 4$.

Compounds with the crystal structure derivative from $Tl^I Tl^{III} Se_2$ (structural type-**III**) can be divided into two groups. The first group (**I**) includes the compounds: $KInTe_2$, $KGaSe_2$, $KInSe_2$, $KGaTe_2$, $KInS_2$, $KTIS_2$, $RbInS_2$, $RbTIS_2$, $CsInS_2$, as well as $CsTIS_2$, for which D varies in the range 0.63-0.92 and $CsGaS_2$ for which D is somewhat above 0.92. It is explained by the fact that the magnitude of the calculated D must be considered somewhat higher for the $A^I GaC_2^{VI}$ compounds than in reality since the ionic radii of the chalcogens in these compounds decrease due to the high polarizability of the Ga^{3+} ion. It has a small radius (0.062 nm) and a high charge. As a result, a part of the electronic density shifts to Ga^{3+} and the ionic radius of the chalcogens in these compounds decreases somewhat. Therefore, for example, $D > 0.63$ for $KGaTe_2$ compound and $D > 0.92$ for $CsGaS_2$ correspondingly.

An analysis of the crystal structure of the compounds of this group and the D values showed that distortion of the structure of the $Tl^I Tl^{III} Se_2$ -type is systematically related to the magnitude of D .

Therefore, the first group of compounds with crystal structure produced from $Tl^I Tl^{III} Se_2$ and $D \geq 0.63$, depending on the D value and their structures, can be divided into four subgroups, such as **Ia**, **Ib**, **Ic**, and **Id** (Table 3).

Subgroup **Ia** contains one compound - $KInTe_2$ with $D = 0.63$, which is isostructural with $Tl^I Tl^{III} Se_2$ and therefore the number of formula units (Z) in the unit cell of the crystal structure is equal to 4.

Subgroup **Ib** consists of the compounds $KGaSe_2$, $KGaTe_2$, and $KInSe_2$ ($0.63 < D \leq 0.71$). The structures of these compounds belong to the triclinic system, which can be regarded as nearly pseudo tetragonal since $\alpha = \beta = \gamma \approx 90^\circ$ [23]. The unit cell is formed as a result of the combination of eight $Tl^I Tl^{III} Se_2$ cells, for which $Z = 32$.

Subgroup *Ic* contains the compounds KInS₂, RbInS₂, CsInS₂, KTlS₂, RbTlS₂, and CsTlS₂, for which $0.71 < D \leq 0.92$. They crystallize in the monoclinic system with a structure close to KFeS₂ [23]. The unit cell is formed as a result of the combination of four Tl^ITl^{III}Se₂ cells, for which $Z = 16$.

For the compound CsGaS₂, $D > 0.92$, and it is classified into subgroup *Id*. Cesium thiogallate crystallizes in the monoclinic system and is isostructural with KFeS₂, $Z = 4$.

The second group of compounds, derivative from Tl^ITl^{III}Se₂, contains NaGaTe₂ and NaInTe₂ for which $D = 0.46$ (Table 3). These compounds are isostructural with Tl^ITl^{III}Se₂, $Z = 4$. For them, anomalies are observed from the general rules. The C.N. of A^I must be 4 or 6 for $D = 0.46$, although the C.N. of A^I is equal to 8 in the reality [23, 24]. This can be explained by the increased metallic fraction of the components of the chemical bonding between the atoms since tellurium participates in the role of C^{VI}. Their structures are "more open" compared to the structure of KInTe₂ and the difference in inter-atomic distances between the values obtained experimentally and determined from the sum of the ionic radii is 0.040 nm for NaGaTe₂, 0.047 nm for NaInTe₂, and 0.020 nm for KInTe₂ (Table 2). As a result of this, the melting points of the NaB^{III}Te₂-type compounds are smaller than the melting points of the KB^{III}Te₂ compounds [6, 16].

Therefore, the structural dependence of the A^IB^{III}C₂^{VI} compounds correlate to the ionic-radii ratios $R_{A^+}/R_{C^{VI}}$ (D), which can be used for predicting the crystal structure of the compounds, which have not been studied yet. Based on this, the crystallographic classification of the A^IB^{III}C₂^{VI} compounds was established. The crystal structures of all the possible compounds of the A^IB^{III}C₂^{VI} - type, including those that have not been studied by now (they are indicated by asterisks, *), are summarized in the Table 3 [6, 16].

The compounds, which have not been studied yet, are placed into the respective groups or subgroups depending upon the magnitude of D . In particular, it is demonstrated that the compounds LiGaSe₂(Te₂), LiInTe₂, LiTlS₂(Se₂, Te₂) must belong to the structural type, produced from ZnS; and NaGaS₂ (Se₂) and NaTlS₂(Se₂) from the structural type, derivative from NaCl, but KGaS₂, RbGaS₂(Se₂, Te₂), CsGaSe₂(Te₂), RbInSe₂(Te₂), CsInSe₂(Te₂), NaTlTe₂, KTlSe₂(Te₂), RbTlSe₂(Te₂), and CsTlSe₂(Te₂) must belong to the structural type, produced from TlSe (Table 3). It should be mentioned that the D values are somewhat higher than the calculated values (as a result of the polarization effect) for the A^IGaC₂^{VI} compounds. The special structures of the thallium compounds should be considered during possible formation of the non-investigated complex thallium compounds in the A^I-B^{III}-C^{VI} systems.

Properties of the A^IB^{III}C₂^{VI} -type compounds, studied by us, as well as those that are described in the literature, are presented in Table 4.

Table 4.

Properties of the $A^{\text{I}}B^{\text{III}}C_2^{\text{VI}}$ - Type Compounds

Compounds	Sum of atomic Numbers, Σz	Melting Points, T , K	References	Density d , g/cm ³	References	Band Gap ΔE , eV	References
Compounds with a crystal structure derivative from ZnS							
LiGaS₂	66	1316	[6, 16]	2.93	[6, 16]	3.8	[6, 16]
LiInS₂	87	1308	[6, 12]	3.44	[6, 12]	3.0	[6, 16]
LiInSe₂	120	1091	[6, 16]	4.50	[16, 21]	2.0	[6, 16]
LiInTe₂	156	935	[6, 16]	5.35	[6, 16]	1.5	[6, 16]
Compounds with a crystal structure derivative from NaCl							
NaGaS₂	74	1225	[28]	2.86	[29]	–	
NaInS₂	92	1193	[6, 12]	4.02	[6, 12]	1.9	[6, 16]
NaInSe₂	128	1153	[9]	5.07	[22]	–	
Compounds with a crystal structure derivative from TlSe							
NaGaTe₂	146	–	–	4.53	[23]	–	–
NaInTe₂	164	893	[9]	4.98	[24]	1.6	[6, 16]
KInTe₂	172	965	[6, 16]	4.99	[24]	–	–
KGaSe₂	118	–	–	4.05	[23]	–	–
KGaTe₂	154	–	–	4.19	[23]	–	–
KInSe₂	136	1211	[6, 16]	4.09	[23]	2.7	[6, 16]
KGaS₂	82	1228	[28]	2.87	[29]	–	–
KInS₂	100	1073	[6, 16]	3.30	[6, 16]	3.0	[6, 16]
RbGaS₂	100	1223	[28]	3.42	[29]	–	–
RbInS₂	118	1373	[3]	3.55	[17]	–	–
CsInS₂	136	1331	[3]	3.95	[3]	–	–
KTlS₂	132	–	–	4.47	[17]	–	–
RbTlS₂	150	–	–	4.49	[17]	–	–
CsTlS₂	168	–	–	5.18	[17]	–	–
CsGaS₂	118	1253	[28]	3.56	[29]	–	–

Based on analyses of the $A^I B^{III} C_2^{VI}$ - type compounds properties (Table 4), it was established that density (d), melting point (T), band gap width (ΔE) depend upon the sum of the atomic number of the elements (ΣZ), which constitute the corresponding compounds, with the definite crystal structural type and the corresponding magnitude of D [6-8, 16]. These correlations are presented in Fig. 5.

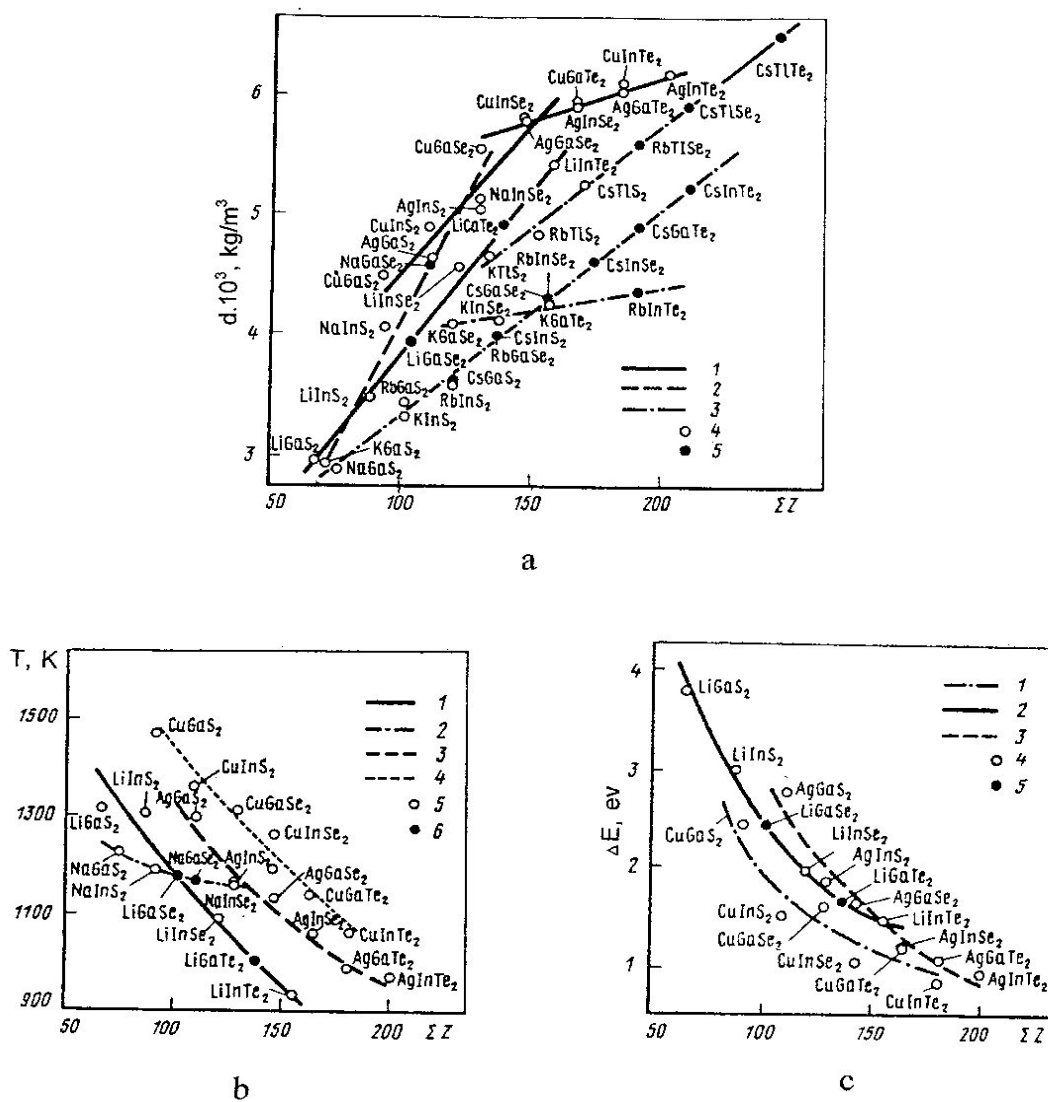


Fig. 5. Dependencies of some parameters of properties of the $A^I B^{III} C_2^{VI}$ - type compounds on the sum of the atomic number of the elements (ΣZ), which constitute the compounds.

- a) Density (d) vs. ΣZ , $d = f(\Sigma Z)$
 - 1, 2 & 3 - Compounds with the crystal structure derivative from corresponding structure types ZnS, NaCl, TlSe.
 - 4 & 5 - Corresponding experimental and predicted data.
- b) Melting points (T) vs. ΣZ , $T = f(\Sigma Z)$
 - 1, 2, 3 & 4 - Corresponding lithium, sodium, silver, copper compounds.
 - 5 & 6 - Corresponding experimental and predicted data.
- c) Band Gap Width (ΔE) vs. ΣZ , $\Delta E = f(\Sigma Z)$
 - 1, 2 & 3 - Corresponding copper, lithium, silver compounds.
 - 4 & 5 - Corresponding experimental and predicted data.

The established correlations can be used for evaluating the properties of the non-investigated compounds. In particular, the density of the compounds (d) varies linearly with Σz for the group of compounds with the same type of structure (Fig. 5a).

An analysis of the melting-point values of the compounds, presented in Table 4, shows that they systematically decrease with increasing Σz for compounds of the same type of structure. The nature of the functional dependency $T = f(\Sigma z)$ changes sharply with the variation of the structural type of the compounds considered here (Fig. 5b). The decrease of the melting points (T) for the compounds with increasing Σz indicates weakening of their stability with increased metallic part of the chemical bonding. This was also confirmed by the decrease of the band-gap widths (ΔE) with increasing Σz (Fig. 5c).

The established functional dependencies can be expressed by the equation of the $Y=[a+b(\Sigma z)]^n$, where $n = 1$ if $Y = d$ and $n = -1$ if $Y = T$ or ΔE (Fig. 5). The a and b coefficients change depending upon the crystal structural type and composition of the compounds, and corresponding value of D , and vary in the ranges: $3.91 \times 10^{-4} \leq a \leq 4.92$; $9.25 \times 10^{-7} \leq b \leq 3.92 \times 10^{-2}$ [6]. These discovered correlations allow to predict some properties of the $A^I B^{III} C_2^{VI}$ -type compounds, which have not yet investigated. The predicted values of the density, melting point, and band gap width for some non-investigated $A^I B^{III} C_2^{VI}$ type compounds are represented in the Table 5.

Table 5.

Predicted Properties for the $A^I B^{III} C_2^{VI}$ Type Compounds

Compounds	Sum of the atomic number of the elements Σz	Density, d g/cm ³	Melting Point, T K	Band Gap, ΔE eV	Compounds	Sum of the atomic number of the elements Σz	Density d g/cm ³
LiGaSe ₂	102	3.93	1161	2.42	CsGaSe ₂	154	4.29
LiGaTe ₂	138	4.91	1008	1.72	CsGaTe ₂	190	4.98
NaGaSe ₂	110	4.45	1174	—	CsInSe ₂	172	4.63
RbGaSe ₂	136	3.95	—	—	CsInTe ₂	208	5.32
RbGaTe ₂	172	4.63	—	—	RbTlSe ₂	186	5.52
RbInSe ₂	154	4.29	—	—	CsTlSe ₂	204	5.88
RbInTe ₂	190	4.32	—	—	CsTlTe ₂	240	6.59

In spite of the isostructural nature of the compounds KTlS₂, RbTlS₂, CsTlS₂, and KInS₂, as well as RbInS₂ and CsInS₂, their functional dependences $d = f(\Sigma z)$ are different, which explains the peculiarities of the electronic structure of thallium atoms, compared to those of gallium and indium. These anomalies need to be taken into account also during the consideration of other properties of thallium-containing compounds.

There is significant scientific and practical interest in the research and application of materials based not only on stoichiometric compounds but also on their solid solutions or more complicated solid solutions such as $A^I B^{III} C_2^{VI} - *A^{I*} B^{III*} C_2^{VI*}$ (the asterisk * marks different elements of the same group). In particular, the $A^I B^{III} C_2^{VI} - *A^{I*} B^{III*} C_2^{VI*}$ solid solutions are new materials and would be very promising for practical applications, where, in this case, A^I - alkaline metal and $*A^{I*}$ - Cu, Ag [6].

The crystal structures and properties of the investigated materials indicate that there are promising semiconductor, electrooptic, nonlinear-optic, luminescence, pyroelectric, piezoelectric materials for

practical applications as frequency converter of I.R. radiation, electrical and photovoltage devices, optical filters, solar batteries, etc. [6, 16].

Conclusions

The discovered correlations allow predicting crystal structure and some properties of the non-investigated $A^I B^{III} C_2^{VI}$ -type compounds. It was found that the crystal structure of $A^I B^{III} C_2^{VI}$ type compounds varies with the magnitude of the ionic-radii ratios $R_{A^+}/R_{C_2^{VI-}}$ (D). The crystallographic classification of these compounds suggests arrangement them into three structural types, such as ZnS-, NaCl-, and TiSe, which enables us to predict the structure of the $A^I B^{III} C_2^{VI}$ compounds, which have not yet been investigated.

For compounds with the same structural type (except for the thallium-containing ones) it was discovered that the density, melting point, and width of the band gap directly depend upon the sum of the atomic numbers of the elements (ΣZ), which constitute the compounds. The decrease in the melting point and the width of the band gap for the compounds with increasing ΣZ indicates weakening of their stability as the metallic component of the chemical bonding increases.

The analysis of this research shows that the formation, crystal structure and properties of materials are determined by the state of materials systems. Correspondingly, the state of a materials system depends upon the established equilibrium of the interconnections among the different chemical and physical factors, such as type and structure of the atoms, chemical bonds and physico-chemical interactions (Fig. 6) [6, 7, 30, 31].

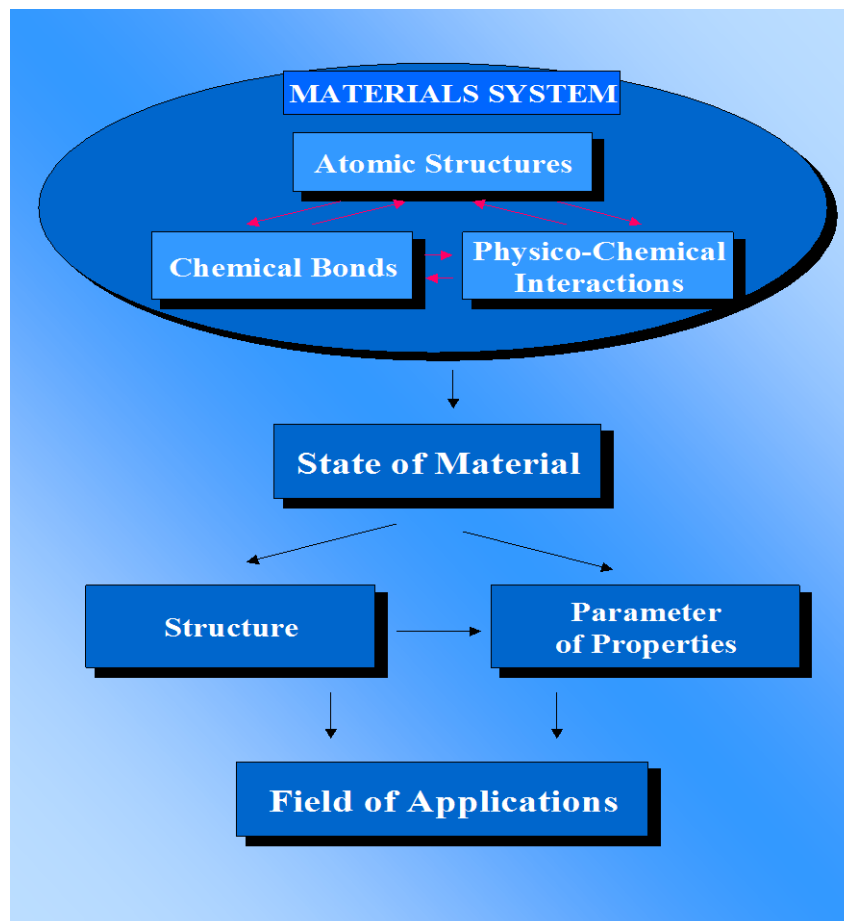


Fig. 6. Interconnections among the different chemical and physical factors in the materials system.

The physico-chemical interactions are determined as interactions among the particles in the materials system by the substance and energy that can be modified by pressure, temperature, radiation or any other type of energy and time duration of applied energy. Accordingly, these interconnections determine the state of matter, i.e. the state of substance, which means a kind of substance and its form of existence (e.g. polycrystalline, single crystal, glass, liquid, gas, plasma states, etc.). Every state of substance has corresponding structure (crystal structure for crystalline materials), i.e. space location of the particles (atoms, ions, molecules) and parameters of properties. Finally, materials structure and parameters of properties determine a field of practical applications.

The understanding of the Material – Process – Crystal Structure – Property – Application relationships, as interconnections among the type and structure of the atoms, chemical bonds and physico-chemical interactions in the materials systems can be used to predict the existence, structure, and properties of the new materials, which have not yet been investigated. In accordance with this approach, it is much easier to find required materials with corresponding properties for specific practical applications and determine the optimum technological treatments in order to get materials in the corresponding forms. This method of the research and development can be used to different materials process and product development. If the market requires a new material for a specific application, the interaction in the materials system could be analyzed in order to determine appropriate materials compositions, state, processes, structure, properties, and design.

References

1. G. D. Boyd, H. M. Kasper, and J. H. McFee, "Linear and nonlinear optical properties of LiInS_2 " J. Appl. Phys., 44, No.6, 2809 (1973).
2. F. J. Negran, H. M. Kasper, and A. M. Glass, "Pyroelectric and electrooptic effects in LiInS_2 and LiInSe_2 " Mater. Res. Bull., 8, 743 (1973).
3. S. K. Kovach, E. E. Semrad, Yu. V. Voroshilov, V. S. Gerasimenko, V. Yu. Slivka, and N. P. Stasyuk, "Preparation and the basic physicochemical properties of alkali-metalindates and -thioindates," Izv. Akad. Nauk SSSR, Neorg. Mater., No. 12, 2172 (1978).
4. N. A. Goryunova, Complex Semiconductors of the Diamond Structure [in Russian], Sov. Radio, Moscow (1968).
5. Ternary Semiconductors of the Diamond Structure [in Russian], Metallurgiya, Moscow (1968).
6. V.B. Lazarev, Z.Z. Kish, E.Yu. Peresh, and E.E. Semrad, Complex Chalcogenides in the $A^I - B^{III} - C^{VI}$ Systems, Publisher - Metallurgiya, Moscow, pp.240, (1993).
7. Z.Z. Kish and E.Yu. Peresh, Physical-Chemical Criterion, Regulations of Formations, and Changes in the Properties of Compounds in the $A^I - B^{III} - C^{VI}$ Systems, in the book: Preparation and Properties of the Complex Semiconductors, Uzhgorod State University, pp. 3-15, Kiev, (1991).
8. Z.Z. Kish, E.Yu. Peresh, and I.E. Barchii, Peculiarities of Formation, Obtaining and Changing Properties of Single Crystals of the $A^I B^{III} C_2^{VI}$ Compounds, in: Abstracts of Papers of the 8th International Conference, Ternary and Multinary Compounds, p.241, Kishinev USSR, (1990).
9. Z.Z. Kish, V.B. Lazarev, Peresh E.Yu., E.E. Semrad, and I.S. Shaplygin, Phase Equilibria in the $A_2^I C^{VI} - \text{In}_2 C_3^{VI}$ Systems, Zh. Neorg. Khim., 30(6), 1499-1501, (1985).
10. Z.Z. Kish, V.B. Lazarev, E.Yu. Peresh, and E.E. Semrad, Compounds in the System $\text{In}_2\text{Se}_3 - \text{K}_2\text{Se}$, Izv. Akad. Nauk SSSR, Neorg. Mater., 24(10), 1602-1605, (1988).
11. V.V. Loshchak, E.E. Semrad, Z.Z. Kish, and E.Yu. Peresh, Phase Equilibria in the $A_2^I S - \text{Ga}_2\text{S}_3$ Systems, in: Abstracts of Papers of the 7th All-Union Conference, Chemistry, Physics, Technology, and Use of the Chalcogenides [in Russian], V.1, p.102, Uzhgorod, (1988).
12. Z.Z. Kish, V.B. Lazarev, E.E. Semrad, E.Yu. Peresh, and I.V. Galagovets, Some Properties of Single Crystals of LiInS_2 and NaInS_2 , Izv. Akad. Nauk SSSR, Neorg. Mater., 20(5), 750-752, (1984).

13. Z.Z. Kish, V.V. Loshchak, E.Yu. Peresh, and E.E. Semrad, Properties of the LiGaS₂ Single Crystals, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 25(12), 1959-1962, (1989).
14. Z.Z. Kish, A.S. Kanishcheva, Yu.N. Mikhailov, V.B. Lazarev, E.E. Semrad, and E.Yu. Peresh, Synthesis and Crystal Structure of Lithium Thioindate LiInS₂, *Doklad. Akad. Nauk SSSR*, 280(2), 398-401, (1985).
15. V.S. D'ordyai, V.A. Stefanovich, E.I. Pan'ko, V.B. Lazarev, E.Yu. Peresh, and Z.Z. Kish, Raman Scattering in LiInS₂, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 24(4), 555-559, (1988).
16. Z.Z. Kish, E.Yu. Peresh, V.B. Lazarev, and E.E. Semrad, Systematics and the Rules of Variations in the Properties of the A^IB^{III}C₂^{VI} - Type Compounds, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 23(5), 777-784, (1987).
17. H. Schubert and R. Hoppe, "Kenntnis der RbInS₂-strukturfamilie," *Z. Naturforsch.*, 25, No.8, 886 (1970).
18. B. K. Vainshtein, V. M. Fridkin, and V. L. Indenbom, *Modern Crystallography*, 2nd edn. [in Russian], Nauka, Moscow (1979), p. 360.
19. W. P. Pearson, *The Physical Chemistry and Physics of Metals and Alloys*, 1st edn., Wiley-Interscience (1972).
20. M. O'Keefe and B. G. Hyde, "Non-bonded interaction and the crystal chemistry of tetrahedral structures related to wurtzite type (B4)," *Acta Crystallogr.*, 34, 3519 (1978).
21. T. Kamijoh and K. Kuriyama, "Single crystal growth and characterization of LiInSe₂", *J. Cryst. Growth*, 51, No.1, 6 (1981).
22. R. Hoppe, W. Lidecke, and F.-K. Frorath, "NaInS₂ and NaInSe₂," *Z. Anorg. Allg. Chem.*, 309, 49 (1961).
23. W. J. Schafer and J. S. Gunter, "Neue ternare Telluride und Selenide der Alkalimetalle mit Elementen der 3 Hauptgruppe," *Z. Naturforsch.*, 31, No. 10, 1336 (1976).
24. E. R. Franke and H. Schafer, "Strukturchemie ternar;r Telluride der Alkali- und Erdalkalimetalle mit den Elementen der 3 Hauptgruppe," *Z. Naturforsch.*, 27, No. 11, 1308 (1972).
25. D. Schmitz and W. Bonger, "Die Xristallstruktur von CsGaS₂" *Z. Naturforsch.*, 30, Nos. 7-8, 491 (1975)
26. M. C. Day and J. Selbin, *Theoretical Inorganic Chemistry*, Van Nostrand Reinhold (1969).
27. N. 1:1. Abrikosov, V. R. Bankina, L. V. Poretskaya, E. V. Skudnova, and S. N. Chizhevskaya, *Semiconductor Chalcogenides and Alloys Based on Them* [in Russian], Nauka, Moscow (1975).
28. P. V. Ivanova, *Chemistry and Technology of Gallium* [in Russian], Metallurgiya, Moscow (1973).
29. B. N. Ivanov-Emin and Ya. I. Rabovnik, "Chemistry of gallium. Hydroxygallates of alkaline and alkaline-earth metals," *Zh. Obshch. Khim.*, Q, 1061 (1947).
30. Z.Z. Kish, *Forms of the State of Matter*, Uzhgorod State University, Uzhgorod, (1989), pp.21, Fig.1, Ref.5, (Monograph [in Russian], Dep. in UkrNIINTI), No.2278-Uk.89, 25.10.1989.
31. Z.Z. Kish, "Advances and Benefits of Newly Developed Ceramics for Industrial Applications", Brochure, ATS Spartec Inc. (2006).