

GLASS FORMATION ABILITY: IS THE RAWSON'S "LIQUIDUS TEMPERATURE EFFECT" ALWAYS EFFECTIVE?

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With the purpose of application of Sun's and Rawson's ideas for evaluation of glass formation in multi-component (and not only oxide) systems, the Sun-Rawson criterion (glass formation ability of oxide is equal to the ratio of the chemical bond energy to the melting temperature in Kelvin), has been modified by replacing the chemical energy with the total covalent-ion binding of the alloy and the melting temperature with the liquidus temperature (the Sun-Rawson-Minaev criterion). It has been shown that the Rawson's "liquidus temperature effect" (increase of glass formation ability with decreasing of the liquidus temperature) in some ranges of phase diagrams of binary glass forming telluride systems As-Te, Ga-Te, Al-Te, which are characterized by "slow slope liquidus line" turned out to be ineffective due to stronger manifestation of the "covalent-ion binding effect" in such regions.

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1. Introduction

Enhanced glass formation ability in regions of phase diagrams of binary systems with decreased liquidus temperature T_{liq} was known since Tamman (1903) [1]. Rawson (1967) [2] has called the effect of increasing of glass formation ability with decreasing of liquidus temperature "the liquidus temperature effect" and expressed the standpoint that glass formation is most probable in eutectic compositions. In 1976 Cornet [3] proposed "the eutectic law" for binary telluride systems forming glasses, in accordance with which glass formation ability (GFA) is maximum for compositions, close to eutectic ones, in telluride systems with elements of III-V groups of the Periodic Table (Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb).

It is interesting that Cornet himself remarked that in some cases compositions with maximum glass formation ability do not coincide with eutectic compositions. For example, in the system Al-Te the eutectic composition contains 23 at.% Al and the maximum glass formation ability has the composition with 24 at.% Al; and, correspondingly, for gallium – 14 and 20 at.% Ga, for thallium – 29.5 and 30% Tl, for As – 27 and 29 at.% As. In his work [3] Cornet did not explain the phenomenon he had revealed.

Hrubý and Stourac [4] have received in the system As-Te glasses in the range of concentrations from 18.80 to 67.55 at.% As and come to the conclusion that GFA, evaluated from DSC data (T_g , T_{cr} , T_m), increases in alloys with increased content of As that also discords with "the eutectic law" as well as with "the liquidus temperature effect" as a whole. In the work of Vengerovich et al. [5] it has been revealed that in systems Al-Te and Ga-Te regions of the most easily glass formation alloys are located some distance away of eutectic compositions shifting in the direction of the chemical compound which forms the eutectic with tellurium.

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2. Glass formation ability and Sun's, Sun-Rawson's and Sun-Rawson-Minaev's (SRM) criteria

The question arises: what is a cause of deviation from the "eutectic law" and the Rawson's "liquidus temperature effect" in glass forming systems As-Te, Al-Te, Ga-Te, Tl-Te?

In our opinion the cause is evident and consists in influence and action of such factor as the energy of chemical bonds between atoms of glass forming alloys on GFA. This cause was revealed first in 1942 by Sun [6] and taken into consideration by Rawson at modification of the Sun's criterion for one-component glasses where the single type of the chemical bond M-O is present. Sun put forward the proposal: the more strong bonds in substance, the slower the process of re-grouping of atoms at transition from liquid to solid state and the easier glass formation. Rawson (1956) [7] proposed to consider at glass formation not only the strength of bonds but also existing thermal energy necessary for their breakage. The measure of such energy is the melting temperature in the case of individual chemical substance (ICS) or the liquidus temperature in the case of multi-component system. The Sun-Rawson's criterion of glass formation ability is the ratio of the bond strength B_{M-O} to the melting temperature in Kelvin. In 1978 Minaev [8] modified the Sun-Rawson's criterion aiming to apply it to chalcogenide and then any other multi-component glass forming systems. According to the quantitative criterion of Sun-Rawson-Minaev (the SRM criterion), glass formation ability of substance is the ratio of the energy of the chemical (as a rule, covalent-ion) binding of the substance (CIB) E_{CIB} , per one averaged atom, to its liquidus temperature in Kelvin at the normal pressure:

$$GFA = \frac{E_{cib}}{T_{liq}} = \frac{\sum E_i M_i K_i / 2}{T_{liq} \sum M_i} \quad (1)$$

where E_i – is the energy of the bond of the certain type, M_i and K_i – the fraction of atoms bounded by this type of chemical bond and valent coordination number of these atoms.

Applications of the SRM criterion facilitated the discovery of some new periodical regularities of glass formation in binary chalcogenide and oxide glass forming systems [9, 10] as well as forecasting and subsequent experimentally revealing new binary and ternary glass forming chalcogenide systems [9, 11, 12].

3. SRM criterion and glass formation in systems As-Te, Ga-Te, Al-Te

Let us consider glass formation in systems As-Te, Ga-Te, Al-Te basing on the SRM criterion.

As-Te system. In accordance with the phase diagram As-Te [13] the liquidus line (Fig. 1) has several dips and rises in the direction from tellurium to arsenic. According to the "liquidus temperature effect" the same dips and rises, but with the reverse sign, should be expected in the glass formation ability at gradual addition of arsenic to tellurium: the steeper the rise of the liquidus, the lesser glass formation ability. However, both Cornet's data (GFA of the composition with 29 at.% As is greater than that of the eutectic with 27 at.% As) and above mentioned experimental data of Hruby and Stourac [4] contradict this expectation. It is obvious that the single temperature factor is not sufficient for evaluation of GFA. It is necessary to add the second factor – the chemical (covalent-ion) binding (CIB) of atoms in alloys.

Calculations of E_{CIB} were carried out based on Pauling's data [14] on energies of chemical bonds $E_{As-As} = 134 \text{ kJ.mol}^{-1}$ and $E_{Te-Te} = 168 \text{ kJ.mol}^{-1}$, the energy of the bond As-Te was calculated using the Pauling's formula:

$$E_{A-B} = \frac{1}{2} (E_{A-A} + E_{B-B}) + 100(X_A - X_B)^2 - 6.5(X_A + X_B)^4 \quad (2)$$

where X_A and X_B – electron negativness factors of chemically interacting elements A and B that are equal (according to Pauling) to 2.0 for As and 2.1 for Te. Calculations give the value of $E_{As-Te} = 152 \text{ kJ.mol}^{-1}$.

Let us give some examples of E_{CIB} calculations:

Composition $As_{20}Te_{80}$. Twenty As atoms form sixty chemical bonds As-Te in which thirty Te atoms take part. The rest 50 Te atoms form 50 bonds Te-Te.

$$E_{CIB} = \frac{152 \text{ kJ.mol}^{-1} \times 60 + 168 \text{ kJ.mol}^{-1} \times 50}{100} = 175.2 \text{ kJ.mol}^{-1}$$

Composition $As_{40}Te_{60}$. Forty As atoms form 120 chemical bonds with sixty Te atoms.

$$E_{CIB} = \frac{152 \text{ kJ.mol}^{-1} \times 120}{100} = 182.4 \text{ kJ.mol}^{-1}$$

Composition $As_{50}Te_{50}$. Fifty Te atoms form one hundred chemical bonds As-Te where $100:1.5=33.3(3)$ As atoms take part. The rest $50-33.3(3)=16.6(6)$ As atoms form $16.6(6) \times 1.5=25$ bonds As-As

$$E_{CIB} = \frac{152 \text{ kJ.mol}^{-1} \times 100 + 134 \text{ kJ.mol}^{-1} \times 25}{100} = 185.5 \text{ kJ.mol}^{-1}$$

Calculations show that E_{CIB} of alloys in the system As-Te (Fig. 1) is a straight-line function in the range from pure Te ($GFA=168 \text{ kJ.mol}^{-1}$) to the composition $As_{40}Te_{60}$ ($E_{CIB}=182.4 \text{ kJ.mol}^{-1}$) and then, also as a straight line but with another slope, from $As_{40}Te_{60}$ to pure As ($E_{CIB}=200 \text{ kJ.mol}^{-1}$). The change of slope in the point $As_{40}Te_{60}$ is explained by the fact that atoms in alloys with the lesser As content are bounded by As-Te and Te-Te bonds, but in alloys with greater As content they are bounded by As-Te and As-As bonds.

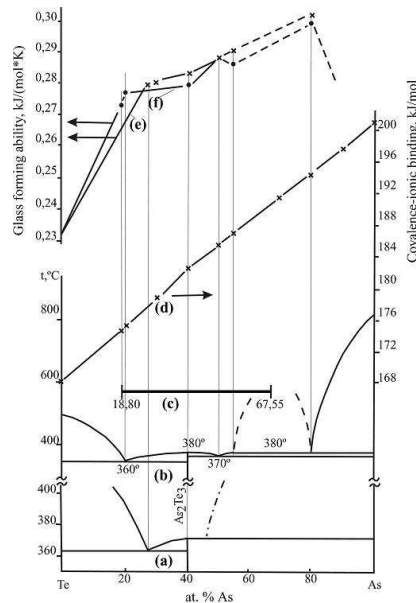


Fig. 1. The phase diagram (a) [3] and (b) [13], the glass formation regions (c) [4], covalence-ionic binding (d) and glass formation ability: (e)– in compliance with phase diagram (a), (f)– in compliance with phase diagram (b) in system As-Te.

The glass formation ability was calculated using the (1) formula. The liquidus temperature and, in particular, eutectic temperatures were determined from phase diagrams (Fig. 1a) proposed by Cornets [15] and from the second more detailed studied diagram of Dembovsky et al. (Fig. 1b) [13]. The GFA calculated from Cornet's data (Fig. 1e) increases sharply in the range from pure tellurium to the eutectic composition $As_{27}Te_{73}$ that completely complies with the Rawson's "liquidus temperature effects" (LTE) – in this range the liquidus temperature (LT) decreases sharply that facilitate increase of GFA. The dependence of the CIB energy upon the composition (Fig. 1d) also increases in this range that, in accordance with SRM criterion also facilitate increase of GFA.

The region of the phase diagram located from the eutectic composition ($As_{27}Te_{73}$) to the chemical compound $As_{40}Te_{60}$ is characterized by slow increase of the liquidus temperature (a "gentle slope", according to Minaev's terminology [16]) and by increase of GFA that contradicts LTE but completely corresponds to the SRM criterion. At the same region, the ion-covalent binding continues to increase with the same intensity as before (the numerator in the formula (1) of the SRM criterion) that leads to increasing of GFA, although less sharp due to the LT increase (Fig. 1e). Here we can observe the effect of "covalent-ion binding" (CIB) that prevails over the LT effect (the denominator in the formula (1) of the SRM criterion) and explains experimentally revealed increasing of glass formation ability [3,4] between the eutectic point and the chemical compound $As_{40}Te_{60}$. The GFA value grows further with increasing of the arsenic content that is in accordance with experimental data of Hruby and Stourac [4] on increasing of GFA in the arsenic-enriched region. Due to the absence of experimental data on GFA in the region of liquid separation, we cannot make any decision on GFA alteration in this region as well as in the region of the liquidus temperature increase with compositions $As_{80}Te_{20}$ – As_{100} . The matter is that the latter region of the phase diagram (Fig. 1b) is characterized by high arsenic vapor pressure and can be obtained only under high pressure which influence on GFA is not documented. Therefore, the alteration of GFA in Fig. 1e and 1f corresponds only formalized calculations and indicated by the dotted line. The proof or disprove of its correspondence to the real GFA requires further experimental works. Bends on the GFA line (Fig. 1e and 1f) are explained well by comparison data on the liquidus temperature in both variants of the phase diagram (Fig. 1a and 1b) and data on alterations of the CIB in the denominator and the numerator in the formula (1) of GFA.

Ga-Te system. Calculations of E_{CIB} and GFA in this system were also made using the SRM criterion. From calculations the following values were taken:

$E_{Ga-Ga} = 180 \text{ kJ}\cdot\text{mol}^{-1}$ [14]. The energy of the bond Ga-Te calculated from the Pauling's formula 2 [14] was equal to $176 \text{ kJ}\cdot\text{mol}^{-1}$. The E_{CIB} in the region from pure Te to the composition $Ga_{40}Te_{60}$ increases $168 \text{ kJ}\cdot\text{mol}^{-1}$ to $213 \text{ kJ}\cdot\text{mol}^{-1}$ (Fig. 2c). The glass formation region lies from the composition $Ga_{15}Te_{85}$ to $Ga_{25}Te_{75}$ [3]. In this system, "effects" of LT, CIB and the fact of suppression of the "liquidus temperature effect" by the "CIB effect" are appeared especially strong (Fig. 2 [16]). At adding gallium to tellurium, the liquidus temperature decreases to the eutectic composition $Ga_{14}Te_{86}$ (Fig. 2a [18,3]) where it is equal to $418 \text{ }^{\circ}\text{C}$. For this composition, according to Cornet [3], glassformation is absent. Then the LT increases and in the point $Ga_{15}Te_{85}$ the glassformation region begins with the maximum GFA for the composition (according to Cornet) $Ga_{20}Te_{80}$. Therefore, at the region $Ga_{14}Te_{86}$ – $Ga_{15}Te_{85}$ the "liquidus temperature effect" is not effective. Calculations of GFA using the SRM criterion (Fig. 2c,d) show the absence of its effectiveness up to the composition $Ga_{24}Te_{76}$. Despite the liquidus temperature increase, at this region GFA increases and the decisive role in its increase is played by the "CIB effect". The glass formation region in this system begins and ends with $GFA = 0.27 \pm 0.01 \text{ kJ}\cdot\text{mol}^{-1}\text{K}^{-1}$, the value that characterizes the minimum glassformation ability of all binary telluride alloys at the cooling rate of $\approx 180 \text{ Ks}^{-1}$ [9,11]. Inside this region, alloys have, naturally, greater glass formation ability that showed calculations illustrated by Fig. 2d. As it can be seen in Fig. 2, in the region from pure Te to the eutectic composition $Ga_{14}Te_{86}$ both factors – "the liquids temperature effect" and "the CIB effect" – "works" to increase GFA, although the result of their cooperative action does not give the minimum GFA which characterizes glass formation. Then, at the gallium content increase, the liquidus temperature increases but the intensity of "the CIB effect" is such that GFA continues to grow, although not so intensive as before (the angle between the GFA line and the horizontal line decreases – Fig. 2d) and reaches the maximum in the composition with 24 at.%Ga content. At Ga

concentration greater than 24 at.%, the GFA sharply decreases due to increasing of the liquidus temperature and the action of "the liquidus temperature effect" becoming stronger again. Here, the like As-Te system prevailing action of "the CIB effect" over the "liquidus temperature effect" is observed in the region of the "slow slope" with compositions 14-24 at.% Ga.

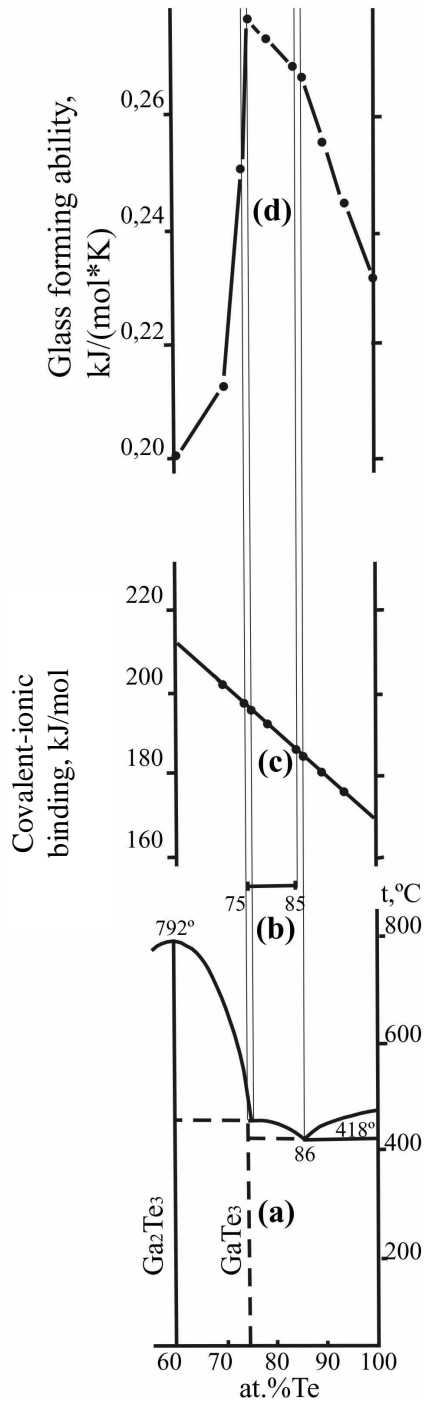


Fig. 2. The phase diagram (a) [18], the glass formation region (b) [3], covalent-ionic binding (c), glass formation ability (d) in system Ga-Te.

Al-Te system. We have found phase diagrams obtained with the time difference of 58 years – Fig. 3a (1917) and Fig. 3b (1975) [3]. The latter diagram gives the liquidus line from pure tellurium to the eutectic composition of 23 at.% Al. Further the liquidus line is indicated by the dotted line (up to the composition with ≈ 30 at.% Al). The glass formation region, according to the same work Cornet [3], lies in the region from 12 to 30 at.% Al (Fig. 3c), the maximum GFA is for the composition $\text{Al}_{24}\text{Te}_{76}$. Calculations of GFA were also carried out using the SRM criterion. The E_{CIB} in this system increases from pure Te ($168 \text{ kJ}\cdot\text{mol}^{-1}$) to the composition $\text{Al}_{40}\text{Te}_{60}$ ($244 \text{ kJ}\cdot\text{mol}^{-1}$) (Fig. 3d), $E_{\text{Al-Al}} = 168 \text{ kJ}\cdot\text{mol}^{-1}$ [17], $E_{\text{Al-Te}} = 203 \text{ kJ}\cdot\text{mol}^{-1}$ (calculations made by the formula (2) of Pauling [14]). The GFA, calculated from both phase diagrams (Fig. 3a and 3b) in the range from pure tellurium to the eutectic composition shows the presence of “the liquidus temperature effect”.

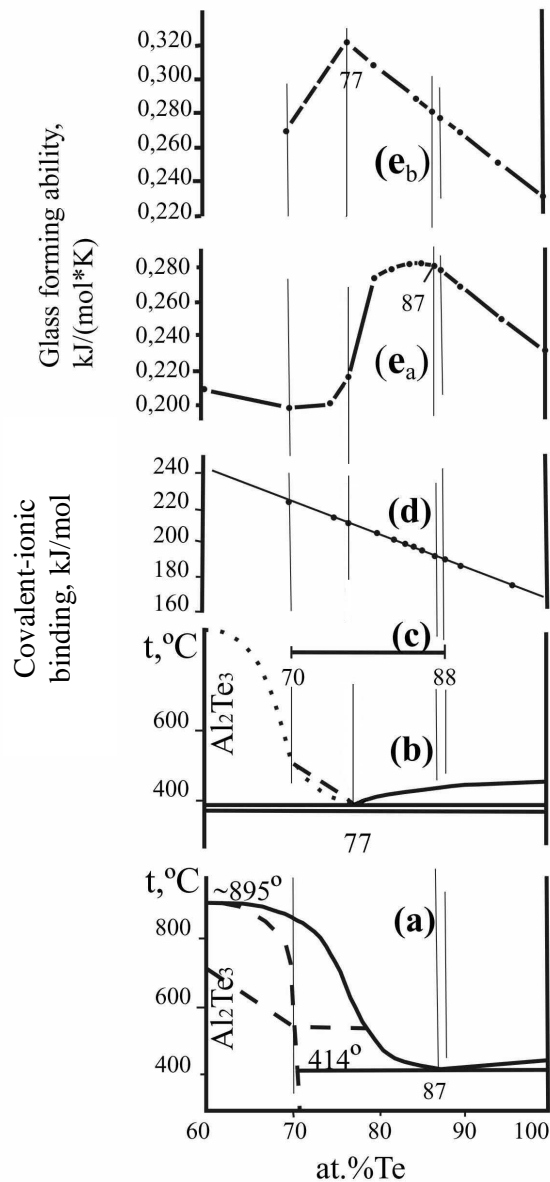


Fig. 3. The phase diagram (a) [19] and (b) [3], the glass formation regions (c) [3], covalence-ionic binding (d) and glass formation ability: e_a – in compliance with phase diagram (a), e_b – in compliance with phase diagram (b) in system Al-Te.

Nevertheless, in the former case ("a") the eutectic composition contains 87 at.%Te and in the latter case ("b") – 77 at.%Te. Further, in the diagram "a" a "slow slope" of the liquidus line is observed at the region from 87 to 84 at% Te. The "liquidus temperature effect" is depressed here by the "CIB effect" and GFA increases. Then, a steeper increase of the liquidus line follows and GFA, firstly slow – to the composition $\text{Al}_{20}\text{Te}_{80}$, and thereafter a sharp decrease is observed. The composition $\text{Al}_{20}\text{Te}_{80}$ has the GFA which is typical, in the limits of experimental spread of values, for boundary glass formation compositions of telluride and the cooling rate of $\approx 180 \text{ Ks}^{-1}$ - $0.27 \pm 0.01 \text{ kJ.mol}^{-1}\text{K}^{-1}$. But the glass formation region stretches further, up to the composition $\text{Al}_{30}\text{Te}_{70}$ for which calculations give the value of $\text{GFA} = 0.20 \pm 0.01 \text{ kJ.mol}^{-1}\text{K}^{-1}$. This result means that data on the liquidus temperature taken from the phase diagram "a" are wrong. None of known systems forms glasses at so small GFA value and the cooling rate of $\approx 180 \text{ Ks}^{-1}$. This is supported by the fact that the phase diagram given by Cornet [3] has the eutectic point with 23 at.%Al, i.e. the high-temperature part of the liquidus line, located on the left-side of the eutectic point, is shifted to the Al-enriched side. It is interesting to note that if the liquidus dotted line is extended and used for calculations, the boundary glass forming alloy has $\text{GFA} = 0.27 \pm 0.1 \text{ kJ.mol}^{-1}$, i.e. it, in fact, coincides exactly with the value of boundary composition of binary telluride glasses obtained at the cooling rate of 180 Ks^{-1} . It means that Cornet's projection, in general, indicates the liquidus line direction correctly, but it does not correspond to his experiment, giving a greater GFA for the composition with 24 at.% Al if compared with the eutectic composition. It seems that from the eutectic point the liquidus line "must" increase more slowly, it "must" have the "slow slope", and after that, at Al content higher than 24 at.% it increases faster, so that to cross the Cornet's dotted line in the point corresponding to the boundary composition $\text{Al}_{30}\text{Te}_{70}$ at $560 \text{ }^\circ\text{C}$.

The above facts and their interpretations allows to suggest that

- 1) the Cornet's phase diagram "a" [3] is more correct than the phase diagram "b" [19];
- 2) the correct liquidus line in the range from $\text{Al}_{23}\text{Te}_{77}$ to $\text{Al}_{40}\text{Te}_{60}$ is likely located in the region which we indicated by dotted-stroke line on the Cornet's phase diagram.

4. Conclusion

1. On the basis of the analysis of experimental data, calculations of the covalent-ion binding and the glass formation ability using the criterion of Sun-Rawson-Minaev, it has been shown on the examples of glass formation systems As-Te, Ga-Te and Al-Te that, in the presence of a slow raising of the liquidus line in the phase diagram of binary system in the direction of increasing of the covalent-ion binding, the CIB effect can neutralize the "liquidus temperature effect", which decreases glass formation ability of alloys in this direction, and, as the result, can enhance the glass formation ability despite the increase of the liquidus temperature.

2. Calculations of glass formation ability using the SRM criterion allow to evaluate critically, semi-quantitatively, the experimental data on the location of liquidus lines in binary phase diagrams and, in the case of several diagrams of the same binary system, to select the diagram which reflects in the most objective way the real location of the liquidus line.

References

- [1] G. Tamman, *Kristalliziren und Schmelzen*, Leipzig, (1903).
- [2] H. Rawson, *Inorganic glass-forming systems*, Academic Press, London and New York (1967).
- [3] J. Cornet, *Proc. of the Sixth Intern. Conf. on Amorphous and Liquid Semiconductors*, 1975, Ed. B. T. Kolomiets, Leningrad, Nauka Publishers, 1976, p. 72.
- [4] A. Hruby, L. Stourac, *Czech. J. Phys. B*, **24**, 1132 (1974).
- [5] R. D. Vengerovich, I. A. Lopatnjuk, V. P. Mikhalchenko, I. M. Kasian, *Proc. 2nd All-Union Conf. "Material Science and Techology of Chalcogenide and Oxide Semiconductors"*, Chernovtsy. USSR, **1**, 150 (1986).
- [6] K. H. Sun, *J. Am. Ceram. Soc.* **30**, 277 (1947).

- [7] H. Rawson, Proc. IV Intern. Congress on Glass, Impremenic Chaix, Paris, 1956, p.62.
- [8] V. S. Minaev, Proc. Intern Conf. "Amorphous Semiconductors – 78", AS ChSSR Publishers, Pardubice- Prague, 1978, p.71.
- [9] V. S. Minaev, Stekloobraznye Poluprovodnikovye Splavy (Glassforming Semiconductor Alloys), Metallurgy Publishers, Moscow (1991).
- [10] V. S. Minaev, S. P. Timoshenkov, V. Z. Petrova, R. R. Khafisov, V. A. Sharagov, Proc. 5th Intern Conf. "Glass Science and Technology for the 21st Century", Prague, Ed. A. Helebrant, M. Mariska, S. Kasa, CD-ROM, 1999, B4-116.
- [11] V. S. Minaev, Elektronnaja Promyshlennost (Electronic Industry), ZNII "Electronica", Moscow, 8(92) – 9(93), 67 (1980).
- [12] V. S. Minaev, Physics and Chemistry of Glass (Russian) **9**, 432 (1983).
- [13] S. A. Dembovsky, I. A. Kirilenko, A. S. Khvorostenko, J. of Non-organic Chemistry (USSR), **13**, 1462 (1968).
- [14] L. Pauling, General Chemistry, W. H. Freeman and Company, San-Francisco (1970).
- [15] J. Cornet, D. Rossier, J. Non-Cryst. Solids **12**, 61(1973).
- [16] V. S. Minaev, Elektronnaja Technika (Electronics Engineering), Seria "Materialy". ZNII "Electronica", **9**, 29 (1980).
- [17] S. Batsanov, Structural Chemistry, Book of Facts (in Russian), Dialog, Moscow (2000).
- [18] P. C. Newman, J. C. Brice, H. C. Wright, Phillips Res. Reports **16**, 41 (1961).
- [19] M. Chikashige, J. Nose, Met. Coll. Sci, Kyoto. Imp. Univ. **2**, 227 (1917).