On general regularity of glass-formation in binary chalcogenide A^{IA}-B^{VIA} and oxide A^{IA}_2O-BxOy systems, where A^{IA} - Li, Na, Ќ, Rb, Cs

Timoshenkov S.P., Minaev V.S.
103460, Moscow, Russia

The common regularity for binary chalcogenide A^{IA}-B^{VIA} and oxide A^{IA}_2O-SiO_2, A^{IA}_2O-P_2O_5, etc. systems has been discovered that consists in regular increasing of glass-formation ability (GFA) and glass-formation regions with increasing of atomic numbers (AN) of A^{IA} elements. GFAs of several chalcogenide and oxide systems have been calculated in intervals of studied parts of phase diagrams in accordance with the San-Rawson criterion, modified by Minaev. The cause of GFA increase at AN increasing has been revealed that consists in regular increase of the ionic component of the chemical bond A^{IA}-B^{VIA} and decrease of the liquidus temperature in this direction.

1. Introduction

In works of pioneers of chalcogenide vitreous semiconductors Gorjunova and Kolomiets [1] the conclusion has been made that in glass-forming chalcogenide systems, which are different from each other by a component of the same subgroup of the Periodic Table (IVA, VA, VIA), the glass-formation region regularly decreases at increasing of the atomic number of the given element.

In works of Minaev, summarized in [2], several inversions of this regularity in chalcogenide glasses have been revealed, for example the inversion "6th period – 5th period" ("5-6"), in particular "Pb-Sn" and "Tl-In", which consists in the fact that at replacement of Sn for Pb or In for Tl in binary and multi-component systems the glass-formation region increases.

Concerning systems A^{IA}-B^{VIA}, it has been already known that in the system Cs_2S-Sb_2S_3 the glass-formation region lies in regions of 0-40 and 65-85 mol.% Sb_2S_3 [3]. It means that Cs_2S has been obtained in glass state. Besides, in the work [4] a tendency of alloys of the Cs-Te system to glass-formation has been revealed at investigations of the phase diagram.

Despite extremely limited experimental material in the Minaev's work [5], the possibility of systematic glass-formation in the whole complex of chalcogenide systems with IA subgroup's elements has been nevertheless considered. The bases of such consideration have been, from one side, above mentioned data, data on presence of glass-formation in ternary systems with alkaline metal based on the As-Se system given in works of Borisova [6] and Dembovsky [7] as well as data of Kokorina and others [8] on glass-formation in Cs_2S-Sb_2S_3 and Rb_2S-Sb_2S_3 systems. From the other side, in the beginning of eighties the structural-energetic concept of glass-formation in chalcogenide glasses [2] has been already worked out as well as the underlied San-Rowson's criterion [9] modified by Minaev and allowed to calculate GFAs for multi-component alloys.

2. Modified glass-formation criterion of San-Rowson

The modified criterion – the San-Rowson-Minaev's criterion (SRM) [2] –allowed to predict and then experimentally reveal glass-formation in a number of new binary and ternary chalcogenide systems and synthesize new semiconductor glasses [10]. In the new SRM criterion the chemical bond energy was replaced for the chemical (covalent-ionic) binding energy of a mole average atoms (E_{cb}) which can be expressed as $E_{cb} = (E_{av}/2)K_{av}$, гДе E_{av} – the average chemical bond energy in alloy; K_{av} – the average valence coordination number of the "average" atom (the average number of covalence-ion bonds per atom). The oxide melting temperature was replaced for the liquidus temperature (T_l) of the given complex alloy expressed in Kelvin. As the result, GFA can be expressed as follows:

$$CC = E_{cb} / T_l = (E_{av}/2)K_{av} / T_l = \Sigma(M_j.K_j.E_j/2) / T_l \Sigma M_j \qquad (1)$$

where: E_j – the bond energy of the given type; K_j – the coordination number of atoms of the given type; M_j – the number of atoms of the given type.

E_{cb} was calculated on the base of energies of chemical bonds $E_{A\text{-}B}$ presented by Pauling [11] and Batsanov [12]. In some cases $E_{A\text{-}B}$ was calculated in accordance with the Pauling's expression [11]:

$$E_{A\text{-}B} = 1/2\,(E_{A\text{-}A} + E_{B\text{-}B}) + 100\,(X_A - X_B)^2 - 6{,}5\,(X_A - X_B)^4 \qquad (2)$$

where: X_A and X_B – electronegativeness of A and B atoms.

3. Features of glass-formation in chalcogenide systems with alkaline metals

Borisova [6] has established the fact of the glass-formation region increase in systems "alkaline metal - As_2Se_3" at increasing of atomic numbers of A^{IA} elements. It was possible to add < 2 at.% Li, 10 at.% Na and up to 30 at.% K to this compound without crystallization.

According to Dembovsky's data [7], the glass-formation region in ternary systems based on As-Se increases in the row Li < Na < K < Rb < Cs. These data are in conflict with the glass-formation regularity in chalcogenide systems with elements of AIII, AIV, AV subgroups of the Periodic Table [1]. In the work of Minaev [5] calculations of glass-formation ability in "alkaline metal – chalcogen" systems were made using the San-Rowson-Minaev's criterion.

The bond energy A^{IA}-B^{VIA} increases at increasing of atomic numbers of chalcogens, for example, kJ/mole: Li – Te 251,2; Na – Te: 252,0; K – Te: 261,9; Rb – Te: 260,4; Cs – Te: 277,3; despite the bond strength between alkaline metal atoms themselves decreases in the same direction – kJ/mole: Li-Li 111; Na-Na 75; K-K 55; Rb-Rb 52; Cs-Cs 45 [11]. This fact is explained by that electronegativeness of alkaline metals decreases at atomic number increasing (Li 1,0; Na 0,9; K 0,8; Rb 0,8; Cs 0,7) [24] causing increase of the electronegativeness difference of the "alkaline metal – chalkogen" couple, the ion component of the bond and its total energy. Data for calculations using liquidus temperatures are taken from known equilibrium diagrams of A^{IA}-B^{VIA} systems [13,14]. Tendency to decreasing of liquidus in the range of alloys with predominant chalcogen content at increasing of atomic numbers of alkaline metals is specific to these diagrams.

Calculations of GFA for systems Na-Te, Rb-Te and Cs-Te (in systems Li-Te and K-Te phase diagrams have not been constructed) show that glass-formation regions must be present at the cooling rate of 180 K/s* at all three systems [5]: in the region of 41-48 at.% Na, 12-27 at.% Rb, 12-46 at.% Cs that makes 7; 13 and 34 at.% correspondingly.

In accordance with the point of view concerning the inversion nature of glass-formation [2], in the case of telluride systems we are apparently dealing with the new type of inversion – the continuous inversion – in inherent to chalcogenide systems regular decrease of GFA at increasing of element atomic numbers [1], with the inversion applied to all elements of the IA subgroup. The tendency to similar inversion is likely to exist in systems with sulfur and selenium as well.

The prediction of glass-formation in binary selenide systems with alkaline metals made in [5] was experimentally confirmed in the work [15] for Cs-Se system. The confirmation of the correctness of the prediction concerning the GFA and glass-formation regions increase at increasing of atomic numbers of alkaline metals in binary chalcogenide systems is similar increase of glass-formation regions in ternary systems with alkaline metals: $A^{IA} – As_2Se_3$ [6], A^{IA} - As - Se [7], A^{IA} - Ge – S [16], A^{IA} - Sb – S [17].

4. Features of glass-formation in $A_2^{IA}O$ - B_xO_y systems

Oxides $A^{IA}{}_2O$ form glasses with B_2O_3, SiO_2, GeO_2, P_2O_5, TeO_2 and other oxides of main subgroups. In systems with SiO_2 [18], GeO_2 [18], P_2O_5 [19] the sufficiently clear tendency of glass-formation region increase at increasing of A^{IA} atomic numbers is observed. For example, in systems with SiO_2 the extension of glass-formation regions is (in mole percents): with Li_2O 34,8; Na_2O 55,0; K_2O 58,0; Rb_2O 59,4; Cs_2O 61,0. Such tendency is significantly less developed in the system with B_2O_3. In systems with TeO_2 the reverse tendency is actually developed. Explanation of features of glass-formation in listed systems requires a serious analysis each of them separately with subsequent generalized consideration of all glass-forming systems.

In this work we will consider in details $A^{IA}{}_2O$ - SiO_2 systems for which the most detailed data on glass-formation were obtained in the work [18]. Glasses were obtained by cooling in air of melt placed in a platinum crucible. Because conditions of glass-formation in all systems are the same, it is obvious that the reason of different ability to glass-formation is in the oxide-modifier and in features of its interaction with the glass-forming oxide.

Unlike chalcogenide systems where the bond energy increases at increasing of atomic numbers due to increasing of the ion part of the covalence bond, the A^{IA}- O bond energy in oxide systems decreases, (insignificantly, though) at increasing of atomic numbers: Li-O 517,1; Na-O 503,1; K-O 501,5; Rb-O 502,2; Cs-O 501,5 (in kJ/mole). Although, like chalcogenide systems, the ion part of the covalence-ion bond increases at increasing of atomic numbers. The covalence-ion binding in $A^{IA}{}_2O$ oxides decreases at increasing of A^{IA} atomic numbers. But the melting temperatures of oxides (Li_20 - 1453 ^0C, Na_20 - 1132 ^0C , K_20 – 740 ^0C, Rb_20 - 505 ^0C [21]) and the liquidus temperature at the phase diagram decreases simultaneously in this row and, as the result, the glass-formation ability of alloys and corresponding the glass-formation regions expand.

Analyzing the $A^{IA}{}_2O$-SiO_2 system on the base of the Sun-Rowson-Minaev criterion and alteration of the chemical bond A^{IA}-O as well as A^{IA}-chalcogen bonds at increasing of atomic numbers of alkaline metals, it can be presumed that the covalent part of the chemical bond A^{IA}-O and its decrease at increasing of atomic numbers are the cause of decrease of melting temperatures of $A^{IA}{}_2O$ and liquidus temperatures in corresponding systems that in accordance with the SRM criterion facilitates increase of the glass-formation ability of alloys. And its ion part increases both the energy of an individual chemical bond and the energy of the total covalence-ion binding of alloy that also increases the tendency to glass-formation.

Basing on results of the above mentioned analysis of GFA from the SRM criterion and extensions of experimental regions of glass-formation, it is possible to predict glass-formation in systems $A^{IA}{}_2O$ with Ga_2O_3, Al_2O_3, As_2O_3 and Sb_2O_3 where glass-formation has not yet been revealed.

Conclusions :

1. Based on the Sun-Rawson-Minaev criterion the prediction is proposed on glass-formation in practically all systems A^{IA}-B^{VIA} as well as the tendency to expansion of glass-formation regions and GFA of these alloys at increasing of atomic numbers of alkaline metals. The new type of inversion ("the continuous inversion") in inherent to chalcogenide systems regular decrease of GFA at increasing of atomic numbers of elements has been revealed.

2. The tendency has been established to increasing of glass-formation regions in binary systems A^{IA}_2O - SiO_2, A^{IA}_2O - GeO_2, A^{IA}_2 - P_2O_5 at increasing of atomic numbers of alkaline metals based on experimental data [18] conformed by calculations of GFA from the SRM-ctiterion.

3. The prediction has been proposed concerning glass-formation in systems A^{IA}_2O with Ga_2O_3, Al_2O_3, As_2O_3, Sb_2O_3 where glass-formation has not yet been revealed.

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