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STUDY ON THE SOLUBILITY KINETICS OF CHALCOGENIDE GLASSES FROM THE As_2Se_3-$GeSe_2$-Ag_4SSe SYSTEM

Venceslav Vassilev[1], **Lilia Aljihmani**[1], **Emilia Fidančevska**[2], **Svetlin Parvanov**[1], **Valeri Vachkov**[3], **Milosav Miloševski**[2], **Temenuga Hristova-Vasileva**[1]

[1]*University of Chemical Technology and Metallurgy, Dept. of Semiconductors,*
8 Kliment Ohridski Blvd., 1756 Sofia, Bulgaria
[2]*Faculty of Technology and Metallurgy, Sts Cyril and Methodius University,*
P.O. Box 580, MK-1001 Skopje, Republic of Macedonia
[3]*South-West University „N. Rilski", Faculty of Mathematics and Natural Science,*
66 Hr. Michailov Blvd., 2700 Blagoevgrad, Bulgaria
venciv@uctm.edu

The solubility kinetics of chalcogenide glasses from the As_2Se_3-$GeSe_2$-Ag_4SSe system waa studied in sodium hydroxide etching solutions. The solubility process at 5, 10, 15 and 20 mass % NaOH in the temperature interval 286 – 352 K is shown. The dependence of solubility rate of glasses on the temperature, concentration of NaOH and composition of the glasses is presented. The main characteristics of the solubility process as a rate of solubility, activation energy and order of reaction were determined.

Key words: chalcogenide glasses; dissolution kinetics; solubility rate; activation energy

ПРОУЧУВАЊЕ НА КИНЕТИКАТА НА РАСТВОРЛИВОСТ НА ХАЛОГЕНИТЕ СТАКЛА ОД СИСТЕМОТ As_2Se_3-$GeSe_2$-Ag_4SSe

Кинетиката на растворливост на халогените стакла од системот As_2Se_3-$GeSe_2$-Ag_4SSe е проучена во раствори за разјадување од натриумхидроксид. Проучен е процесот на растворливост при 5, 10, 15 и 20 mas % NaOH во температурен интервал од 286 до 352 K. Прикажана е зависноста на брзината на растворливост на стаклата од температурата, концентрацијата на NaOH и составот на стаклата. Одредени се главните карактеристики на процесот на растворливост – брзината на растворливост, енергијата на активација и редот на реакција.

Клучни зборови: халогени стакла; кинетика на растворување; брзина на растворливост; енергија на активација

INTRODUCTION

The use of the chalcogenide glasses (ChG) as protective layers for some elements in the optoelectronics, as well as active component in the preparation of electronic elements, requires the knowledge of the chemical stability of the glasses. The dissolution kinetics of ChG in acidic and alkaline media has been studied by many authors [1–3].

The ion-built solids, in which the building particles are connected by distant-reacting electrostatic culone powers, dissolve easier (require smaller activation energy of the dissolution process E_a) than the covalent ones, because the particles are connected harder in the latter (require larger E_a). The dissolution rate of the ion-built solids is limited by the velocity of the diffusion processes in solution and in the covalent-built solids – by the velocity of the physico-chemical reaction on the borders between the solid and liquid phases. The chemical bond in ChG is practically covalent. The ionic-component of the chemical bond is insignificant.

When investigating the solubility of the As-Se and As-S glasses in NaOH solutions at temperatures 15–45 °C, it is determined that the glasses with stoichiometric proportions of the components are the most stable and the dissolution rate in that case is defined by the chemical reaction on the surface of the solid phase, as the value of activation energy is 63–84 kJ/mol. When dissolving glasses with non-stoichiometric component proportions, a noticeable influence of the diffusion on the dissolution rate is observed and it is determined that As_2Se_3 groups are passing in the solutions, and the solid phase responds to a As_2Se_4-composition [1]. In the glasses with a small As-content (up to 20 at. %), Se-fragments are etched with priority and in the glasses containing As over 20 at. % As_2Se_3 passes into the alkaline solution [2].

In the glasses from the Ge-Se system the covalent constitution of the chemical bond is close to that of Ge in the glassy As_2Se_3. Because of that reason the dissolution rate in the glassy Ge-chalcogenides is limited by the heterogenic chemical reaction on the border surface.

When adding Ge to the ChG of the binary systems As-Se and As-S, with the characteristic trigonal and chain $AsSe_{3/2}$ and $AsS_{3/2}$ structures, respectively, the more conservative tetrahedral $GeSe_{4/2}$ and $GeS_{4/2}$ structures are formed in the composition of the glasss. When additing Ge in the glassy alloys $AsSe_x$ and AsS_x, their chemical stability will increase. When investigating the solubility of ChG $AsS_{1,5}Ge_x$, $AsS_{2,5}Ge_x$ and $AsSe_{1,5}Ge_x$ in 5N NaOH at 25 °C, it is determined that there is a noticeable decrease in the dissolution rate at Ge-content in the ChG ≥ 17–20 mol %, i.e. when the concentration of the tetrahedral and the trigonal structural units become commensurable. The As-Ge-Se ChG are chemically more steady in respect to the dissolution in alkalis, compared to the As-Ge-S ChG with the same content of Ge, because the tri-dimensional $AsSe_{3/2}$ structure is stronger than $AsS_{3/2}$, on one hand, and the ionic constitution of the As-S chemical bond is bigger than this of the As-Se bond [4], on the other. Besides, the proportion of the structural units $GeSe_{4/2}$ and $AsS_{3/2}$ does not have substantial influence on the solubility of ChG As-Ge-Se [1].

The addition of metallic alloys to the arsenic-selenide and germanium-selenide ChG has influence on the chemical stability of the glass. In many ways the chemical stability increases when metallic components are added: Tl, Cu, Bi, Mn, Fe, Co, Ni [1], Ga and Sn [5].

The aim of the present work was to investigate the dissolution kinetics of ChG from the $(As_2Se_3)_x(GeSe_2)_y(Ag_4SSe)_z$ system in NaOH solutions and determine some of the parameters characterizing this process.

In the $(As_2Se_3)_x(GeSe_2)_y(Ag_4SSe)_z$ system, where $x + y + z = 1$ and $m = y/(x + y)$, there exists As_2Se_3-rich ChG. The glass-forming region (Fig. 1), lies fully on the As_2Se_3-$GeSe_2$ side and partially on the As_2Se_3-Ag_4SSe side (from 0 to 25 mol% Ag_4SSe). In the Ag_4SSe-$GeSe_2$ system glasses were not obtained [6].

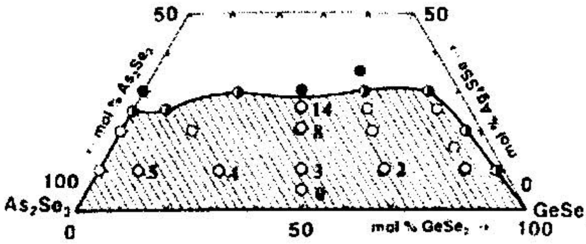

Fig. 1. Glass-forming region in the As_2Se_3-$GeSe_2$-Ag_4SSe system [6]

The ChG from the As_2Se_3-$GeSe_2$-Ag_4SSe system seems to be interesting concerning the possibility of their use as protective layers, as well as active material for ion-selective membranes, waveguides, gas-sensors, etc. The initial components of these ChG are typical semiconductor compounds: As_2Se_3 and $GeSe_2$ are classical glass-formators. As_2Se_3 is frequently used for construction of optical devices [7, 8]. Ag_4SSe is a narrow-gap semiconductor, synthesized for the first time by Earley [9]. It has very good thermo-electrical properties [10, 11].

EXPERIMENTAL:

The synthesis of the initial components, as well the glasses from the system is well described previously [6]. The position of the investigated samples in the Gibbs concentration triangle is shown on Fig. 1.

From the synthesized samples, by cutting, grinding and polishing, volumetric solids with a suitable form were produced, giving the possibility for the determination of their full surface. The samples were dissolved in NaOH solution (5, 10, 15 and 20 mass %) at temperatures in the range 285–351 K. The temperature has been set and held with the help of a thermostat type Ultra NBE (Fig. 2), and the dissolution process was executed in a connected to it electrochemical cell (Fig. 3). For better temperature control of the working process and minimizing the influence of the diffusion rate when dissolving the ChG, a magnetic mixer have been used at a spinning rate of 250 rev/min (as determined experimentally).

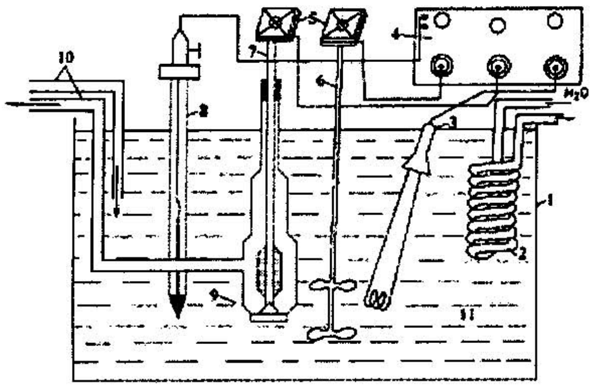

Fig. 2. Experimental set of a thermostat:
1) thermostat type Ultra NBE; 2) cooler; 3) heater; 4) electrical switchboard; 5) electrical engine; 6) mixer; 7) water-supercharger propeller; 8) contact thermometer; 9) pump; 10) inlet and outlet orifice; 11) heating (cooling) fluide for the electrochemical cell

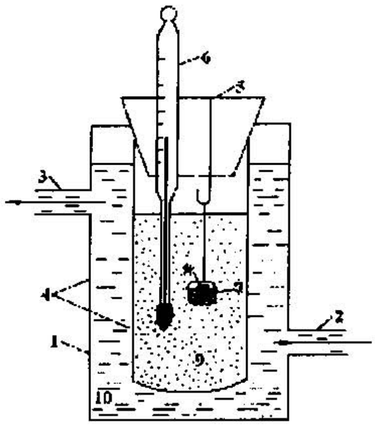

Fig. 3. Electrochemical cell scheme:
1) electrochemical cell; 2 and 3) inlet and outlet orifice; 4) internal and external walls of the electrochemical cell; 5) rubber gasket with a holder; 6) precise thermometer; 7) chemically resistive metallic basket; 8) investigated sample; 9) etching (working) solution; 10) heating (cooling) fluid

The overall dissolution rate is determined by the velocity of the particular stages: transport of the solvent towards the reaction surface; chemical reaction; leading off the products of the reaction from the reaction surface. The limiting stage is the one that is the slowest. If the rates of the different stages are comparable, the process passes in the transitional area and its velocity is determined by the diffusion rate, as well as the heterogeneous chemical reaction rate, passing on the boundary surface. For every following series of measurements a "fresh" solution of NaOH is used.

The samples were placed in a basket made by a cantal wire, inert on the etching solution in the investigated temperature interval. The solution temperature was measured with a mercury thermometer (with accuracy ± 0.1 °C). After reaching equilibrium state (T = const) the basket with the sample was introduced in the electrochemical cell (Fig. 3). Two series of measurements were led:

Series 1: At T_1, T_2, T_3 and T_4 (C = 20 % NaOH);

Series 2: At C_1, C_2, C_3 and C_4 (T = 286 K).

RESULTS

For determination of the dissolution rate of the glass, the equation $w = \frac{\Delta m}{S \cdot M \cdot \Delta t}\ (\frac{\text{mol}}{\text{cm}^2/\text{s}})$ was used, where w – dissolution rate; Δm – weight difference before and after the dissolution; S – area of the sample; M – average molecular mass; Δt – dissolution time [12]. The results are shown in Table 1.

For determination of the activation energy of the dissolution process, the dependence $-\ln w = f(10^3/T)$ (Fig. 4) is built, by which, with the help of the $\ln w = -A(1/T) + B$ equation [13], the activation energy (E_a) is determined. As an example, on Fig. 4, the experimentally received dependence $-\ln w = f(10^3/T)$ for one of the investigated samples is shown (it is similar for the others samples). The obtained values of E_a are summarized in Table 2.

The results from the investigation of the influence of NaOH-concentration are shown in Table 3 and an illustration of the dissolution rate dependence is shown on Fig. 5 (it is similar for the other samples).

The order of the reaction n [4] is determined on the basis of the $\ln w = f(C)$ dependence and the $w = kC_1^{n_1}C_2^{n_2}C_i^{n_i}$ (i = 1, 2, ..., m) equation, where k is the velocity constant of the reaction.

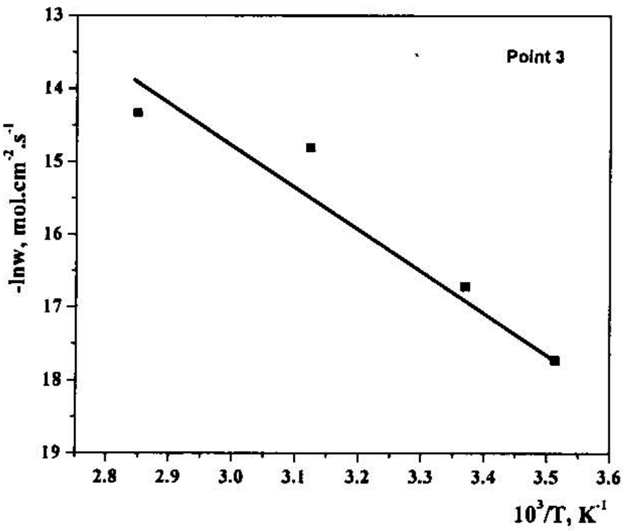

Fig. 4. Dependence of the dissolution rate and the temperature for sample with composition $(As_2Se_3)_{45}(GeSe_2)_{45}(Ag_4SSe)_{10}$

Table 1

Dissolution rate of the samples from the $(As_2Se_3)_x(GeSe_2)_y(Ag_4SSe)_z$ system

Samp.	T K	S cm^2	m_1 g	m_2 g	Δm g	t s	w mol/cm^2·s
3	284.6	0.6201	0.0792	0.0767	0.0025	600	$2.0\cdot10^{-8}$
	296.8	0.8505	0.1262	0.1168	0.0094	600	$5.5\cdot10^{-8}$
	320.2	0.5724	0.1055	0.0850	0.0205	300	$3.7\cdot10^{-7}$
	351.1	0.9160	0.1493	0.0942	0.0551	300	$6.0\cdot10^{-7}$
4	284.6	0.6004	0.0593	0.0567	0.0026	600	$2.0\cdot10^{-8}$
	296.8	0.7010	0.1042	0.0902	0.0140	600	$9.2\cdot10^{-8}$
	320.2	0.9843	0.1701	0.1300	0.0401	300	$3.8\cdot10^{-7}$
	351.1	0.6031	0.0703	0.0391	0.0312	300	$4.8\cdot10^{-7}$
8	284.6	1.0368	0.1013	0.0990	0.0023	600	$1.0\cdot10^{-8}$
	296.8	0.7783	0.1240	0.1167	0.0073	600	$4.4\cdot10^{-8}$
	320.2	0.7636	0.0945	0.0777	0.0168	300	$2.1\cdot10^{-7}$
	351.1	0.6804	0.0855	0.0562	0.0293	300	$4.0\cdot10^{-7}$
14	284.6	0.6364	0.0681	0.0651	0.0030	600	$2.1\cdot10^{-8}$
	296.8	0.5425	0.0795	0.0678	0.0117	600	$9.8\cdot10^{-8}$
	320.2	0.7536	0.1062	0.0864	0.0198	300	$2.4\cdot10^{-7}$
	351.1	0.5950	0.1011	0.0673	0.0338	300	$5.2\cdot10^{-7}$
0	284.6	0.5863	0.0433	0.0403	0.0030	600	$2.7\cdot10^{-8}$
	296.8	0.4752	0.0638	0.0559	0.0079	600	$8.7\cdot10^{-8}$
	320.2	0.5254	0.0597	0.0457	0.0140	300	$2.8\cdot10^{-7}$
	351.1	0.6475	0.1019	0.0742	0.0277	300	$4.4\cdot10^{-7}$
2	284.6	0.5110	0.0625	0.0616	0.0009	600	$9.7.\ 10^{-9}$
	296.8	0.6520	0.0821	0.0779	0.0042	600	$3.5\cdot10^{-8}$
	320.2	0.4480	0.0506	0.0445	0.0061	300	$1.5\cdot10^{-7}$
	351.1	0.5184	0.0921	0.0686	0.0235	300	$5.0\cdot10^{-7}$
5	284.6	0.8446	0.1161	0.1133	0.0028	600	$1.4\cdot10^{-8}$
	296.8	0.9504	0.1429	0.1298	0.0131	600	$6.0\cdot10^{-8}$
	320.2	0.7830	0.0938	0.0766	0.0172	300	$1.9\cdot10^{-7}$
	351.1	0.6804	0.0869	0.0571	0.0325	300	$3.9\cdot10^{-7}$

Table 2

Values of the activation energy E_a for samples of the As_2Se_3-$GeSe_2$-Ag_4SSe system

Sample	A	$-B$	E_a, kJ/mol
3	5000.7	+ 0.00	41.7
4	4921.9	+ 0.00	41.0
8	5077.1	− 0.01	42.1
14	4944.6	+ 0.01	41.1
0	4936.0	+ 0.02	41.0
2	5119.4	− 0.05	42.6
5	5051.8	+ 0.00	42.1

Table 3

Values of the reaction order and the dissolution rate depending on the NaOH concentration at $T = 286$ K

Samp.	T s	S cm^2	m_1 g	m_2 g	Δm g	W mol/(cm^2·s)	C %	n
3	600	0.1444	0.0592	0.0592	0	–	5	1.34
	600	0.2025	0.0843	0.0829	0.0014	$3.47\cdot10^{-8}$	10	
	600	0.2304	0.0626	0.0605	0.0021	$4.58\cdot10^{-8}$	15	
	600	0.2116	0.0731	0.0683	0.0048	$1.14\cdot10^{-7}$	20	
4	600	0.5328	0.0470	0.0467	0.0003	$1.01\cdot10^{-8}$	5	1.09
	600	0.2116	0.0903	0.0898	0.0005	$2.20\cdot10^{-8}$	10	
	600	0.2500	0.1082	0.1052	0.0030	$5.55\cdot10^{-8}$	15	
	600	0.2025	0.0271	0.0244	0.0027	$6.17\cdot10^{-8}$	20	
8	600	0.0900	0.0433	0.0431	0.0002	$1.04\cdot10^{-8}$	5	1.21
	600	0.1806	0.0842	0.0830	0.0012	$3.12\cdot10^{-8}$	10	
	600	0.1444	0.0491	0.0475	0.0016	$5.20\cdot10^{-8}$	15	
	600	0.2025	0.0438	0.0416	0.0022	$5.09\cdot10^{-8}$	20	
14	600	0.1225	0.0558	0.0554	0.0004	$1.48\cdot10^{-8}$	5	1.49
	600	0.2025	0.0583	0.0572	0.0011	$2.47\cdot10^{-8}$	10	
	600	0.2025	0.0749	0.0712	0.0037	$8.29\cdot10^{-9}$	15	
	600	0.1681	0.0527	0.0486	0.0041	$1.11\cdot10^{-7}$	20	
0	600	0.1225	0.0340	0.0335	0.0005	$2.12\cdot10^{-8}$	5	1.02
	600	0.1296	0.0463	0.0450	0.0013	$5.22\cdot10^{-8}$	10	
	600	0.1024	0.0399	0.0374	0.0025	$1.27\cdot10^{-7}$	15	
	600	0.1156	0.0561	0.0542	0.0019	$8.55\cdot10^{-8}$	20	
2	600	0.8769	0.0484	0.0470	0.0014	$8.76\cdot10^{-9}$	5	1.68
	600	0.1600	0.0624	0.0614	0.0010	$3.43\cdot10^{-8}$	10	
	600	0.0961	0.0362	0.0354	0.0008	$4.56.\ 10^{-8}$	15	
	600	0.2025	0.0598	0.0560	0.0038	$1.03\cdot10^{-7}$	20	
5	600	0.1225	0.1013	0.1008	0.0005	$1.75\cdot10^{-8}$	5	0.69
	600	0.1444	0.1092	0.1078	0.0014	$4.16\cdot10^{-8}$	10	
	600	0.1521	0.0642	0.0623	0.0019	$5.36\cdot10^{-8}$	15	
	600	0.3200	0.0463	0.0433	0.0030	$4.02\cdot10^{-8}$	20	

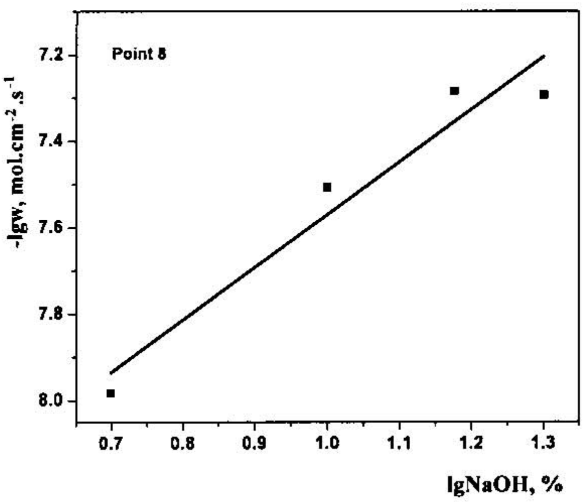

Fig. 5 Dependence of the dissolution rate and the concentration of NaOH at $T = 286$ K for a sample with composition $(As_2Se_3)_{40}(GeSe_2)_{40}(Ag_4SSe)_{20}$

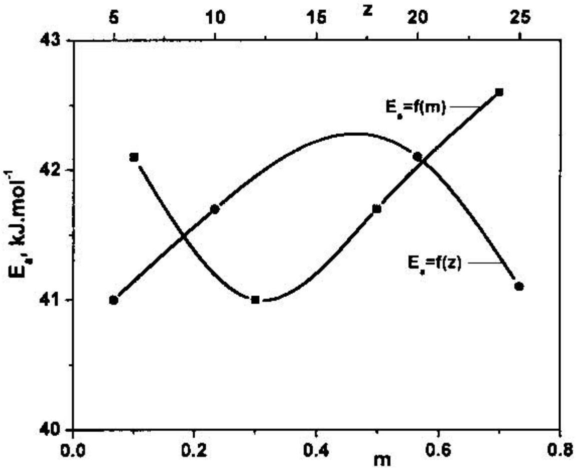

Fig. 6 Alternation of E_a in dependence of the glass composition $(As_2Se_3)_x(GeSe_2)_y(Ag_4SSe)_z$: $E_a = f(m)$ at $z = 10$ mol % Ag_4SSe; $E_a = f(z)$ at $m = 0{,}5$

DISCUSSION

Influence of the temperature on the kinetic characteristics

In the investigated temperature range 286–352 K the dissolution rate logically increased with the raising of T (Table 1).

When adding of $GeSe_2$ to the glasses $(As_2Se_3)_{90}(Ag_4SSe)_{10}$, together with the characteristic for them trigonal structural units $AsSe_{3/2}$, in the volume of the new glasses $(As_2Se_3)_{90-u}(GeSe_2)_u(Ag_4SSe)_{10}$ new tetrahedral structural units $GeSe_{4/2}$ are formed, in which the atoms are covalently bound. That leads to an increase of the chemical stability of the ChG. In the primary moment (at low concentrations of $GeSe_2$), the influence of the tetrahedrons is intangible. The structure of the glass obviously becomes more untidy, with more defects keeping the dominant influence of the trigonal structural units, and the dissolution rate raises (E_a decreases). When the $GeSe_2$ content in the ChG reaches $u \geq 20$ ($m \geq 0.22$) the influence of the tetrahedrons becomes limited and the dissolution rate decreases (E_a increases) (Fig. 6).

With the increase of the Ag_4SSe content in the $(As_2Se_3)_x(GeSe_2)_y(Ag_4SSe)_z$ system up to $z = 20$ mol % the dissolution rate decreases, and after that it begins to increase (E_a passes through a maximum at $z \approx 20$ mol %). Most probably at $x > 20$ mol %, a concentration which is very close to the glass-forming boundary, a formation of the crystalline phase Ag_4SSe starts, very fine disperguized in the glasses, which leads to breach of its homogeneity.

From the surface of the dissolving glass micro-aggregates are broken off, in fact these are weakly connected between themselves streaks of Ag_4SSe, which fall into the sediment without dissolution and the alkaline solution starts to dissolve faster the Ag_4SSe-poored glass (E_a harshly decreases at $z \geq 20$ mol % Ag_4SSe).

The closer values of the activation energy are a proof that the chemistry of the dissolution of the investigated samples from the $(As_2Se_3)_x(GeSe_2)_y(Ag_4SSe)_z$ system is practically identical. That provides the reason to average the experimental data of E_a (Table 3). The average value is 41.6 kJ/mol ($\approx$ 10 kcal/mol). The limiting stage in the dissolution of the glasses $(As_2Se_3)_x(GeSe_2)_y(Ag_4SSe)_z$ in NaOH is the chemical process at the boundary surface, since $\overline{E}_a \geq 10$ kcal/mol [14].

Influence of the concentration on the kinetic characteristics

With the increase of the NaOH concentration, the w of the samples raises (Table 4 and Fig. 5). In the $w(C)$-dependence minimum or saturation tendency are not observed, i.e. during the dissolution processes, leading to passivation of the surface do not occur. The location of the experimental points gives the reason to presume that the linear course of the dependence $-\lg w = f(C)$ would be kept at least to concentrations of NaOH of the order of 35 – 40 %. Over these values the diffusion from and towards the sample's surface will render more stronger influence, due to the continuously increasing viscosity of the solution, independently of the high mixing rates.

At low concentrations of NaOH ($C_{NaOH} < 5$ %) the investigated samples did not dissolve.

At constant Ag_4SSe concentration and increase of the $GeSe_2$ content, the dissolution rate (w) decreases and this tendency is kept up to $C_{NaOH} = 15$ % (Fig. 7). Here, as in the dependence w (T), the addition of the first quantities $GeSe_2$ (at low values of "m") the chemical stability of the glasses increases, since new structural units $GeSe_{4/2}$ with strong tetrahedral bonds appear. In parallel with this tendency another one is developing, which opposes the first the structure of the glass becomes more untidy, more defective at keeping the dominant influence of the $AsSe_{3/2}$-tetrahedrons and w depends more weakly of m and at $m \geq 0.5$, w practically does not change, even a tendency of increase of w "arises" with the increase of the $GeSe_2$-content. At $C_{NaOH} = 20$ % that tendency is even stimulated. At this concentration of NaOH another curious experimental fact is observed. At $m \geq 0.5$ w strives for saturation with a tendency of decrease. This is most probably connected to a surface passivation, as a result of the very good adhesion of the products on it, which makes their quick transition in the solution impossible, independently of the high mixing rate.

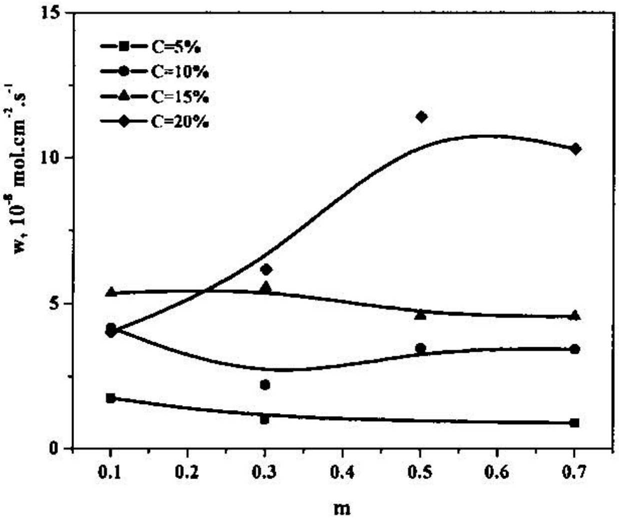

Fig. 7. Dependence $w = f(m, C_{NaOH})$ at $z = 10$ mol %

The dependencies $w = f(z, C_{NaOH})$ at m = const. are exceptionally interesting (Fig. 8). The dissolution rate of the glasses in the solutions containing 5 and 10 % NaOH "logically" changes: it increases with the increase of C_{NaOH} and with a decrease of z. At $C_{NaOH} = 15$ % the curve, which expresses the $w(z)$ dependence, "bends" and a plateau in the range $0.3 \leq m \leq 0.5$ appears. At $C_{NaOH} = 20$ % this tendency becomes stronger and the dependence $w(z)$ approaches to the sinusoidal one. In the above-mentioned mechanism for dissolution of these glasses, two tendencies were shown, which have influence in contrary directions on the variation of w. When the influence of the Ag_4SSe concentration on the w is examined, another tendency must be supplemented, a result from the fact that this compound does not dissolve in NaOH. With the increase of the Ag_4SSe-content, w will decrease, but in parallel the As_2Se_3 and $GeSe_2$ are "washed" from the surface of the glass and the glass becomes richer of Ag_4SSe, than the volume is. That leads to formation of the crystalline phase Ag_4SSe, which temporarily passivates the surface and impedes the dissolution. When a critical quantity of the crystalline phase is accumulated, it tears from the surface of the dissolving glass and passes into the sediment without dissolution. The alkaline solution starts to dissolve more quickly the glass, poored of Ag_4SSe. The cyclic recurrence of these processes reflects also on the course of w (Fig. 8), $C = 20$%. Here w is to be understood as the average velocity, which is a sum of few addents, characterizing the different phases (stages) of the dissolution. They, on their side, are strongly dependent on the concentration of the particular glass' components and their chemical nature, on the concentration of the solvent, in this case NaOH, on the structure of the glass and its dispersity, etc.

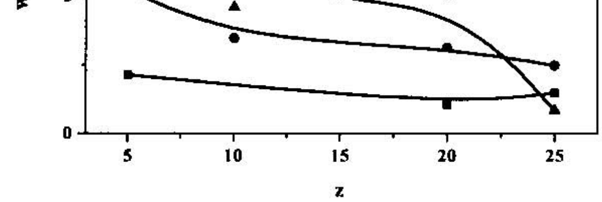

Fig. 8. Dependence $w = f(z, C_{NaOH})$ at $m = 0.5$

A correlation between the reaction order n and the glass composition exists. The dependencies $n = f(m)$ at z = const. and $n = f(z)$ at m = const. most probably have a linear nature with a positive angle coefficient (Table 3) (the values of n were calculated individually for every composition).

If it is assumed that the chemistry of dissolution from one composition to another in the boundaries of one system and for one solvent is approximately identical, an average value of the chemical reaction order ($\overline{n}$) would be mentioned. For determination of $\overline{n}$, the same method as for determination of n is used, but instead of $\ln w = f(\ln c)$ the dependence $\overline{w}_{c_i} = f(\ln c_i)$ is built, where $\overline{w}_{c_i} = \left(\Sigma w_{j,c_i}\right)/N : j = 1, 2, 3.....N$; N – number of the investigated compositions from the system (in the concrete case $N = 7$ – Table 3; $i = 1, 2, 3...K$; K – number of used solutions, in which the dissolution is to be led; w_{j,c_i} – dissolution rate of the j-sample in solution with a concentration c_i; $\overline{w}_{c_i}$ – average dissolution rate in solution with a concentration c_i. The initial experimental data is taken from Table 3 and the values of $\overline{w}_{c_i}$, needed for the calculation of $\overline{n}$, are presented in Table 4.

Table 4

Average values of the chemical reaction order and of the dissolution rate for $(As_2Se_3)_x(GeSe_2)_y(Ag_4SSe)_z$ glasses in NaOH

C %	$\overline{w}_{c_i}$ 10^{-8} mol/cm^{2}s	$\overline{n}$
5	1.38	
10	3.44	1.31
15	6.60	
20	8.09	

If in the process of certain chemical reaction the solid phase takes place (as is in the current case), its concentration does not participate in the law of mass action and the dissolution rate of the heterogenous reaction is $w = -dC/d\tau = k \cdot C^{n}_{\mathrm{NaOH}}$. The analysis of the $w(C)$-dependence and the obtained value for $\overline{n}$ ($1 \le \overline{n} \le 2$ – Table 4) show that during the dissolution of the As_2Se_3-$GeSe_2$-Ag_4SSe glasses in NaOH complicated chemical reactions are passing, consising of two or more simple (one-staged) reactions, connected by one or another way. Most probably they are consecutive (with a formation of transitional compounds) and parallel (passing in two or more directions) reactions. In the composition of the glass three components are included. As it was mentioned before, Ag_4SSe do not dissolve in NaOH. It is very likely that the dissolution of As_2Se_3 and $GeSe_2$ passes in parallel and each of these compounds dissolves consecutively with a formation of transitional products: As_2O_3, SeO_2 and GeO_2.

CONCLUSIONS

As a result of the investigations taken, the following generalized conclusions could be made:

1. The dissolution rate in the $(As_2Se_3)_x(GeSe_2)_y(Ag_4SSe)_z$ increases with the raising of the temperature (from 284 to 351 K) and with the increase of the concentration of NaOH (from 5 to 20 %), and depends on the composition. The average dissolution rate at 351 K is $4.8 \cdot 10^{-7}$ mol/cm^{2}s (at 10 % NaOH). The average dissolution activation energy of the glasses in NaOH is 41.7 kJ/mol.

2. A correlation between the dissolution rate, the temperature and the concentration of the solution, on one hand, and the composition of the glasses, on the other, is determined.

3. The dissolution rate of the glasses in NaOH is limited by the heterogeneous chemical reaction on the surface of the samples. The average value of the chemical reaction order ($\overline{n}$) is 1.3.

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