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REGULARITIES OF GLASS FORMATION AND THERMAL STABILITY OF GLASSES IN THE MF_2 — MS — Ga_2S_3 (M = Mg, Ca, Sr, Ba) SYSTEMS

SUMMARY. The glass transition area limits for the samples in the MF_2 — MS — Ga_2S_3 (M = Mg, Ca, Sr, Ba) systems are determined by the experiment. The areas of the glass-forming in ternary systems adjoin to the binary MS — Ga_2S_3 systems and spread increasing the content of alkaline-earth metal fluoride. The Zachariasen's rule confirms that the increase in the radius of the alkaline-earth metal contained in the glass results in improving the ability of melts to vitrify. The symptomatic temperatures of the glasses formed in the systems are calculated by the differential-thermal analysis. The criteria of their thermal stability are calculated as follows: the T_g/T_l ratio (the Kauzman's rule); $\Delta T = T_x — T_g$; $H_r = (T_x — T_g)/(T_l — T_x)$ (the Khruby's criterion); $H` = (T_x — T_g)/T_g$ (reduced glass transition temperature); $S = ((T_c — T_x)(T_x — T_g))/T_g$ (the Saade-Pule's equation). It is demonstrated that fluorine-sulfide glasses have higher thermal stability than similar sulfide glasses. The average values of thermal stability criteria for fluorine-sulfide glasses are 1.5-2 times as much as the ones of corresponding sulfide glasses. When the radius of alkaline-earth metal increases, the thermal stability of sulfide and fluorine-sulfide glasses tends to decrease. Some physicochemical and optical features of synthesized sulfide and fluorine-sulfide glasses based on Ga_2S_3 are given.

KEY WORDS. Gallium sulfide, chalcogenide glass, symptomatic temperature, thermal stability.

Introduction. Optical materials based on chalcogenide glasses (CGG) are of particular interest for fiber optics and semiconductor technologies. The increased CGG application is caused by their high transparency in the infrared (IR) spectrum, the non-occurrence of high-energy backgrounds in their vibration spectrum, the occurrence of high refractive index (> 2.1) and semiconducting properties [1], and, what is important, the high resistance to aggressive environment. Based on them, high-efficiency lasers, amplifiers, IR radiation converters can be successfully developed.

There is no published data on glass-forming and thermal stability of the Ga_2S_3 based fluorine-sulfide glasses. In [2] there is the mathematical calculation of the glass-forming ability of the covalent melt carried out by the method [3], [4], basing on the quantum characteristics of atoms in the given melt and taking into account the nature of the interaction between them.

The purpose of this paper is to detect the glass transition area limits, to determine the symptomatic temperatures and the criteria of thermal stability of glasses formed in the MF_2 — MS — Ga_2S_3 (M = Mg, Ca, Sr, Ba) systems by an experiment.

The experiment. To test the theoretical glass transition area limits of the melts in the MF_2 — MS — Ga_2S_3 (M = Mg, Ca, Sr, Ba) systems by an experiment, the samples were synthesized with 10 mol. % increments, and with 5 mol. % increments near the glass transition area limits. The glass was produced when the initial sulfide or fluorine-sulfide batch corresponding to the stoichiometric composition of the pre-evacuated and sealed quartz ampoules (residual pressure of 0.01 - 0.001 Pa). The melt mass was soaked during 20 minutes and then chilled by dropping the melt ampoule into cold water. The X-ray amorphism of produced glass was monitored by the XRF method using the *DRON-3M* and *DRON-6* X-ray diffraction meters in the CuK_α (Ni-filter) and CoK_α (Fe-filter) filtered radiation. All X-ray patterns of produced glasses look like amorphous samples. The evenness of the glass was monitored visually by the inside-light inspection using the microscope at x200 magnification. The symptomatic temperatures were determined by the differential-thermal analysis (DTA) at the rate of heating samples of 15 K / min (Al_2O_3 was used as a reference standard), the error in the temperature determination did not exceed ± 3K. The pycnometric specific gravity of glasses was measured with toluene as the pycnometric liquid. The microhardness was determined by the *PMT-3M* microhardness tester, the indenter load was 10 g. The optical band gap was calculated according to the wavelength of the blue edge of the absorption band for glass samples according to the equation ΔE (eV) = 1.24 / λ (μm) [5].

Results and discussion. Fig. 1 demonstrates the theoretically calculated [2] and the experimentally determined glass transition area limits of the samples in the MF_2 — MS — Ga_2S_3 (M = Mg, Ca, Sr, Ba) systems. The areas of glass forming in the systems adjoin to the MS — Ga_2S_3 (M = Mg, Ca, Sr, Ba) binary system. The amount of fluoride added to the sulfide systems causing glass formation regularly increases with the increase in the alkaline-earth metal radius, that results in remarkable increase in the glass transition area and, thus, in a higher glass-transition tendency of the melts in the range of from the magnesium systems to the barium ones.

This regularity confirms one of the Zachariasen's glass formation rules [6] stating that the glass formation tendency should increase with the increase in the ionic radius of mono- or divalent modifying cation in the glassy network. This rule, formulated for oxide glasses, proved to be true for fluorine-sulfide glasses. Perhaps, it is caused by the slight changes in the glass anion subnetwork when the transition from oxide glasses to fluorine-sulfide ones occurs due to the proximity of the electronic anion structure ($2s^22p^6$ for O^{2-} and F^-, $3s^23p^6$ for S^{2-}) and the effective ionic radii (r (O^{2-}) = 0.135 nm, r (F^-) = 0.1285 nm; r (S^{2-}) = 0.184 nm) [7], [8].

The thermal stability criteria are significant for glasses. Some criteria based on symptomatic temperatures are used to quantify the glass thermal stability: glass transition temperatures (T_g), early crystallization temperatures (T_x), exothermic crystallization peak maximum temperatures (T_c), system liquidus point (T_l). In a first approximation, the measure of glass thermal stability is the T_g/T_l value, determined by the Kauzman's empirical rule or by the "two thirds rule", when for the most of the glass-forming systems in a wide range of temperatures (up to 2,000 K) and the melted sample cooling rate from 10^{-2} to 10K/sec, the $T_g/T_l \approx 2/3$ condition is true [9]. Thereby, the decrease in this ratio is interpreted as a decreased glass-transition tendency of the system. The larger this value is, the higher the glass-forming ability of the system and the slower is the crystallization process near T_g is. In addition to this ratio, to quantify the glass thermal stability, the difference between the early crystallization temperatures and the glass-transition ones: $\Delta T = T_x — T_g$, the Khruby's criterion: $H_r = (T_x — T_g)/(T_l — T_x)$, the reduced glass-transition temperature: $H` = (T_x — T_g)/T_g$, and the criterion calculated by the Saade-Pule's equation: $S = ((T_c — T_x)(T_x — T_g))/T_g$ are used. The increase in these values indicates the increase in the glass thermal stability [10], [11] and [12].

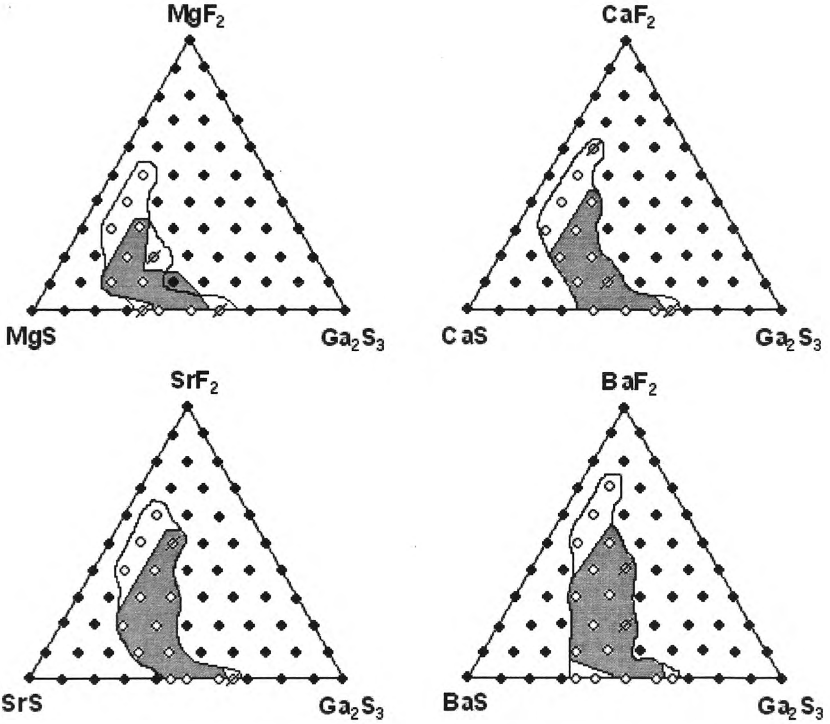

Fig. 1. The predicted and experimentally determined glass transition areas of the melted samples in the MF_2 — MS — Ga_2S_3 (M = Mg, Ca, Sr, Ba) systems:
○ — glass transition at spontaneous cooling;
Ø— glass transition at high chilling rates; ● — no glass transition;
▨ — the experimentally determined glass transition area of the melted samples.

Table 1

The values of the symptomatic temperatures and the thermal stability criteria for glasses formed in the MF$_2$ — MS — Ga$_2$S$_3$ (M = Mg, Ca, Sr, Ba) systems

The composition of the glass, mol. %	T_g, K	T_x, K	T_c, K	T_l, K	T_g/T_l	ΔT, K	H_r	H\`	S, K
50MgS-50Ga$_2$S$_3$	870	978	1,013	1,365	0.64	108	0.28	0.12	4.34
60MgS-40Ga$_2$S$_3$	860	985	1,025	1,350	0.64	125	0.34	0.16	5.81
10MgF$_2$-50MgS-40Ga$_2$S$_3$	755	980	1,002	1,120	0.67	225	1.61	0.30	6.56
30MgF$_2$-50MgS-20Ga$_2$S$_3$	773	994	1,030	1,130	0.68	221	1.63	0.29	10.29
10MgF$_2$-60MgS-30Ga$_2$S$_3$	795	985	1,017	1,145	0.69	190	1.19	0.24	7.65
20MgF$_2$-60MgS-20Ga$_2$S$_3$	797	976	1,098	1,160	0.69	179	0.97	0.22	27.40
10MgF$_2$-70MgS-20Ga$_2$S$_3$	812	975	1,093	1,180	0.69	163	0.80	0.20	23.69
40CaS-60Ga$_2$S$_3$	850	996	1,040	1,432	0.59	146	0.33	0.17	7.56
50CaS-50Ga$_2$S$_3$	845	982	1,020	1,388	0.61	137	0.34	0.16	6.16
60CaS-40Ga$_2$S$_3$	863	1000	1,037	1,336	0.65	137	0.41	0.16	5.87
40CaF$_2$-40CaS-20Ga$_2$S$_3$	777	995	1,072	1,140	0.68	218	1.50	0.28	21.60
10CaF$_2$-50CaS-40Ga$_2$S$_3$	765	993	1,067	1,176	0.65	228	1.26	0.30	22.05
20CaF$_2$-50CaS-30Ga$_2$S$_3$	775	987	1,069	1,180	0.66	212	1.10	0.27	22.43
30CaF$_2$-50CaS-20Ga$_2$S$_3$	755	986	1,082	1,210	0.63	231	1.03	0.31	29.37
10CaF$_2$-60CaS-30Ga$_2$S$_3$	778	992	1,075	1,230	0.63	214	0.90	0.28	22.83
20CaF$_2$-60CaS-20Ga$_2$S$_3$	785	996	1,070	1,225	0.64	211	0.92	0.27	19.89
40SrS-60Ga$_2$S$_3$	820	980	1,017	1,300	0.63	160	0.50	0.20	7.22
50SrS-50Ga$_2$S$_3$	840	940	979	1,275	0.66	100	0.30	0.12	4.64

The composition of the glass, mol. %	T_g, K	T_x, K	T_c, K	T_l, K	T_g/T_l	ΔT, K	H_r	H`	S, K
$55SrS-45Ga_2S_3$	850	955	1,000	1,270	0.67	105	0.33	0.12	5.56
$50SrF_2-30SrS-20Ga_2S_3$	755	962	1,010	1,150	0.66	207	1.10	0.27	13.16
$30SrF_2-40SrS-30Ga_2S_3$	743	976	1,005	1,143	0.65	233	1.40	0.31	9.09
$40SrF_2-40SrS-20Ga_2S_3$	740	961	997	1,150	0.65	221	1.17	0.30	10.75
$10SrF_2-50SrS-40Ga_2S_3$	767	960	998	1,133	0.68	193	1.12	0.25	9.56
$20SrF_2-50SrS-30Ga_2S_3$	793	944	1,007	1,170	0.68	151	0.67	0.19	12.00
$30SrF_2-50SrS-20Ga_2S_3$	800	984	1,011	1,160	0.69	184	1.05	0.23	6.21
$10SrF_2-60SrS-30Ga_2S_3$	760	958	1,003	1,142	0.67	198	1.08	0.26	11.72
$20SrF_2-60SrS-20Ga_2S_3$	815	990	1,015	1,190	0.68	175	0.88	0.21	5.37
$40BaS-60Ga_2S_3$	847	971	1,010	1,460	0.58	124	0.25	0.15	5.71
$50BaS-50Ga_2S_3$	870	945	992	1,413	0.62	75	0.16	0.09	4.05
$40BaF_2-30BaS-30Ga_2S_3$	760	950	987	1,200	0.64	190	0.76	0.25	9.25
$50BaF_2-30BaS-20Ga_2S_3$	797	935	982	1,162	0.69	138	0.61	0.17	8.14
$20BaF_2-40BaS-40Ga_2S_3$	745	953	990	1,200	0.62	208	0.84	0.28	10.33
$30BaF_2-40BaS-30Ga_2S_3$	735	957	1,002	1,165	0.63	222	1.07	0.30	13.59
$40BaF_2-40BaS-20Ga_2S_3$	773	954	998	1,162	0.66	181	0.87	0.23	10.30
$10BaF_2-50BaS-40Ga_2S_3$	830	942	988	1,220	0.68	112	0.40	0.13	6.21
$20BaF_2-50BaS-30Ga_2S_3$	845	950	993	1,240	0.68	105	0.36	0.12	5.34
$30BaF_2-50BaS-20Ga_2S_3$	815	937	980	1,190	0.68	122	0.48	0.15	6.44
$10BaF_2-60BaS-30Ga_2S_3$	860	956	989	1,270	0.68	96	0.30	0.11	3.68

According to the DTA results for the glasses in the MS — Ga_2S_3 (M = Mg, Ca, Sr, Ba) systems, the T_g, T_x values are within the range of 820-870 K and 940-1,000 K, respectively, the difference (T_x — T_g) is 75-160 K (Table 1). The melting is one- or two-stage.

To increase the glass-transition ability of covalent melts and, thus, to decrease the crystallization ability (T_x — T_g) of glasses forming in the MS — Ga_2S_3 (M = Mg, Ca, Sr, Ba) systems, it was proposed to add the suitable low-melting component to the initial sulfide batch. Alkaline-earth metal fluorides have low melting temperatures, they are transparent in the IR spectrum, so they are optimal for solving the task set, with the cationic glass composition and, hence, its structure remaining. The glass formation in the ternary MF_2 — MS — Ga_2S_3 (M = Mg, Ca, Sr, Ba) systems was studied on the cross-sections of the tetrahedra with the constant fluoride composition of MF_2 — 10, 20, 30, 40 mol. %, according to the theoretical calculations (Fig. 1).

The forming fluorine-sulfide glasses are more resistant to crystallization; according to the DTA data, the glass transition temperatures (T_g) are within 740-860 K, and the $\Delta T = T_x — T_g$ values are 96-233 K, depending on the glass composition, that exceeds the corresponding values for sulfide glasses (Table 1). The melting of fluorine-sulfide glasses is mainly two-stage, sometimes, it is three-stage.

According to the calculations presented in Table 1, the following regularities are obtained. The T_g/T_l ratio for sulfide glasses is from 0.58 to 0.67, for fluorine-sulfide glasses it is from 0.62 to 0.69, which correlates well with the "two-thirds" rule (the Kauzman's rule). Thus, the increase in the Tg/Tl ratio for fluorine-sulfide glasses against the sulfide ones indicates the increased glass transition tendency of fluorine-sulfide melts and, thus, the increased thermal stability of the fluorine-sulfide glasses obtained.

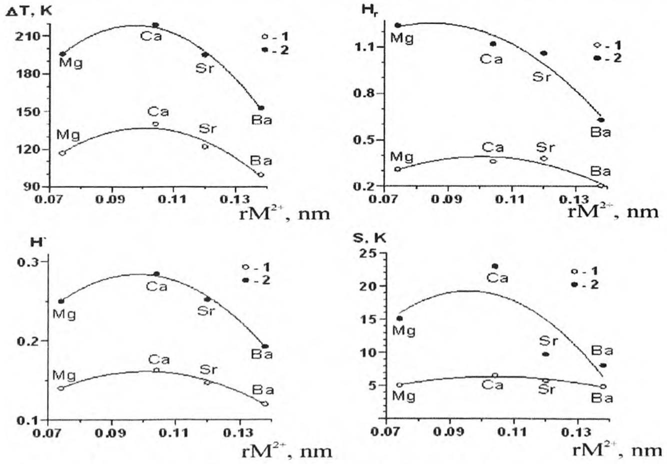

Fig. 2. The dependence of the averaged values of the glass thermal stability criteria in the MS — Ga_2S_3 (1) and MF_2 — MS — Ga_2S_3 (M = Mg, Ca, Sr, Ba) (2) systems on the ionic radius of the alkaline-earth element

The averaged values of the thermal stability criteria for sulfide glasses are 1.5-2 times lower than those of fluorine-sulfide glasses (Fig. 2), which suggests that the thermal stability of sulfide glass increases when alkaline-earth metal fluorides are added. If the H_r value for the sulfide glass is lower than 0.5, i.e. if special cooling conditions must be chosen for glasses to be obtained, then the H_r values for fluorine-sulfide glasses are close to or higher than 1.0 (except for most of the glasses formed in the BaF_2 — BaS — Ga_2S_3 system). This indicates that fluorine-sulfide glasses can be obtained in spontaneous air cooling of melts and they have higher thermal stability. The highest values of the Khruby's criterion (H_r) were obtained for the samples having the lowest values of the liquidus temperature, i.e. for those which have the composition near the triple eutectic points in the MF_2 — MS — Ga_2S_3 systems.

Table 2 demonstrates some of the physicochemical and optical features of the synthesized sulfide and fluorine-sulfide glasses based on Ga_2S_3.

Table 2

Some parameters of the physicochemical and optical features of glasses in the MF_2 — MS — Ga_2S_3 (M = Mg, Ca, Sr, Ba) systems

System	$\rho_{pycn.}$, g/cm^3	H, MPa	Band gap E_g, eV	Transparency, %	
				Optical region	IR region
MS – Ga_2S_3	2.8-3.0	1,300-2,200	3.02-2.75	50-70	50-65
MgF_2–MgS–Ga_2S_3	3.6-3.9	2,300-2,500	2.95-2.98	70-80	70-85
CaF_2–CaS–Ga_2S_3	3.1-3.3	1,900-2,000	2.63-2.53	80-90	75-90
SrF_2–SrS–Ga_2S_3	3.0-3.25	1,800-2,000	2.92-2.97	80-90	80-95
BaF_2–BaS–Ga_2S_3	2.6-2.7	1,500-1,700	2.25-2.38	70-85	70-80

Conclusion. The glass transition area limits in the MF_2 — MS — Ga_2S_3 (M = Mg,Ca, Sr, Ba) systems are determined by the experiment. The symptomatic temperatures of the glasses formed in the systems are determined by the differential-thermal analysis, and the criteria of their thermal stability are calculated. The Zachariasen's rule confirms that the increase in the radius of the alkaline-earth metal contained in the glass results in improving the ability of melts to vitrify. It is demonstrated that fluorine-sulfide glasses have higher thermal stability than similar sulfide glasses. When the radius of alkaline-earth metal increases, the thermal stability of glasses tends to decrease.

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