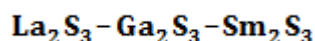




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STUDY OF SYNTHESIS AND GLASS FORMATION IN THE SYSTEM

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The boundaries of glass-formation area in the $\text{La}_2\text{S}_3 - \text{Ga}_2\text{S}_3 - \text{Sm}_2\text{S}_3$ system have been located using simultaneous thermal analysis, X-ray diffraction, and X-ray microanalysis. The physical-chemical properties and thermal decomposition, as well as the IR spectrum of glass compositions $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.20}(\text{Sm}_2\text{S}_3)_{0.20}$ and $(\text{Ga}_2\text{S}_3)_{0.55}(\text{La}_2\text{S}_3)_{0.15}(\text{Sm}_2\text{S}_3)_{0.30}$ were examined. It was determined that the glass composition $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.20}(\text{Sm}_2\text{S}_3)_{0.20}$ at 865 K is resistant to ambient oxygen. In the IR spectrum of the bands of glasses characterizing the Me–S bond, the intensity is increased and shifted to the high-frequency side of the spectrum in comparison with the initial crystal components, which is probably due to the increased covalence of the Me–S bonds.

Keywords: physical-chemical properties, IR spectrum, thermal decomposition, chalcogenides, lanthanides

INTRODUCTION

Glass-based materials are known to have the smallest absorption coefficient in the wavelength range of practical interest. Chalcogenide glasses doped with lanthanide ions are highly competitive with other alternatives in the fabrication of optical devices. There is currently intensive research effort aimed at raising the hardness of materials, reducing their brittleness, improving their thermal stability, and extending their transmission range. In this respect, lanthanide sesquisulfides are promising materials [1-8]. The presence of gallium sulfides in the composition of glass is known to improve lanthanide solubility. The mechanism of this effect is as follows: The gallium ion is a strong Lewis acid. Because of this, owing to an additional (fourth) bond it forms stable complex structural units involving lanthanides, thereby helping to obtain a uniform distribution of them over the glass network [9-15]. This effect has been observed in both chalcogenide and oxychalcogenide glasses.

The objectives of this work were to locate the likely boundary of the glass-forming region in the $\text{La}_2\text{S}_3 - \text{Ga}_2\text{S}_3 - \text{Sm}_2\text{S}_3$ system and study some physicochemical properties of new phases synthesized in this system.

MATERIAL AND METHODS

In the $\text{La}_2\text{S}_3 - \text{Ga}_2\text{S}_3 - \text{Sm}_2\text{S}_3$ quasi-ternary system, samples were synthesized [16] from the primary components ($\beta - \text{Ga}_2\text{S}_3$, $\alpha - \text{La}_2\text{S}_3$ and $\alpha - \text{Sm}_2\text{S}_3$) to determine the boundaries of the glass formation area. 9 of them correspond to the concentration plane of the quasi-binary system $\text{Ga}_2\text{S}_3 - \text{La}_2\text{S}_3$, and 5 $\text{Ga}_2\text{S}_3 - \text{Sm}_2\text{S}_3$.

The synthesis was carried out at 1425 K in a “steclographic” buta placed in a quartz reactor under sulfur pressure for 2.5 hours. The rapid cooling process was performed by immersing the reactor directly in water at room temperature from the synthesis temperature.

In the Ga_2S_3 – Sm_2S_3 quasibinary system, the color of the glass changes from dark yellow to orange. In the quasi-ternary system La_2S_3 – Ga_2S_3 – Sm_2S_3 , the color of the sample containing $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.40}$, which is rich in La_2S_3 , changes from yellow to dark orange as the amount of Sm_2S_3 increases (Fig. 1).



Fig. 1. Photograph of glass with the composition $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.20}(\text{Sm}_2\text{S}_3)_{0.20}$

RESULTS AND DISCUSSION

Synthesized triple $(\text{Ga}_2\text{S}_3)_{1-x}(\text{La}_2\text{S}_3)_{x-y}(\text{Sm}_2\text{S}_3)_y$ glass is resistant to air, water, organic solvents at room temperature, alkaline and mineral partially decomposes under the influence of acids, completely dissolves in the chromium mixture when heated.

In the Ga_2S_3 – Sm_2S_3 system $(\text{Ga}_2\text{S}_3)_{0.71}(\text{La}_2\text{S}_3)_{0.29}$; $(\text{Ga}_2\text{S}_3)_{0.70}(\text{La}_2\text{S}_3)_{0.30}$; $(\text{Ga}_2\text{S}_3)_{0.65}(\text{La}_2\text{S}_3)_{0.35}$; $(\text{Ga}_2\text{S}_3)_{0.61}(\text{La}_2\text{S}_3)_{0.39}$; $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.40}$ respectively 4.1005; 4.1181; 4.2082; 4.2830 and 4.3022 g/cm³.

Densities of glasses with the composition

$(\text{Ga}_2\text{S}_3)_{0.65}(\text{La}_2\text{S}_3)_{0.30}(\text{Sm}_2\text{S}_3)_{0.05}$; $(\text{Ga}_2\text{S}_3)_{0.65}(\text{La}_2\text{S}_3)_{0.25}(\text{Sm}_2\text{S}_3)_{0.10}$;

$(\text{Ga}_2\text{S}_3)_{0.65}(\text{La}_2\text{S}_3)_{0.20}(\text{Sm}_2\text{S}_3)_{0.15}$; $(\text{Ga}_2\text{S}_3)_{0.65}(\text{La}_2\text{S}_3)_{0.15}(\text{Sm}_2\text{S}_3)_{0.20}$;

$(\text{Ga}_2\text{S}_3)_{0.65}(\text{La}_2\text{S}_3)_{0.10}(\text{Sm}_2\text{S}_3)_{0.25}$; $(\text{Ga}_2\text{S}_3)_{0.65}(\text{La}_2\text{S}_3)_{0.05}(\text{Sm}_2\text{S}_3)_{0.30}$ obtained by replacing in the glass with the composition $(\text{Ga}_2\text{S}_3)_{0.65}(\text{La}_2\text{S}_3)_{0.35}$ while keeping the amount of Ga_2S_3 constant La_2S_3 with Sm_2S_3 respectively 4.0573; 4.0816; 4.1064; 4.1314; 4.1566; 4.1822 g/cm³.

The boundaries of the glass forming region in the La_2S_3 – Ga_2S_3 – Sm_2S_3 quasi-ternary system were determined by the methods of physicochemical analysis – X-ray diffraction, REM, EDX, DTA, DTG and STA (Fig. 2 $m_1m_2m'_1m'_2$ area). On the sides $(\text{La}_2\text{S}_3$ – Ga_2S_3 ($m_1m'_1$)) and Ga_2S_3 – Sm_2S_3 ($m_2m'_2$)) of the La_2S_3 – Ga_2S_3 – Sm_2S_3 quasi-ternary system the glass formation area exists at concentrations around the corresponding nonvariant equilibrium [17].

In Figure 2, the dark-colored visually transparent glass area is bounded on both sides by a hatched strip that characterizes the visually opaque glass on both sides in the triple system.

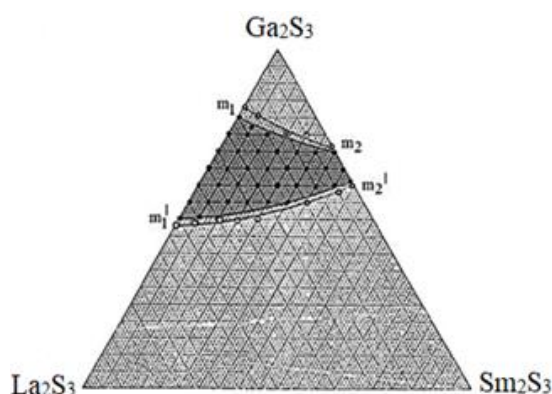


Fig. 2. Glass-forming region in the La_2S_3 – Ga_2S_3 – Sm_2S_3 system

The diffraction patterns of the alloys in a quasi-ternary La_2S_3 – Ga_2S_3 – Sm_2S_3 system were carried out by X-ray diffraction and compared with the initial components are given in figures 3 and 4.

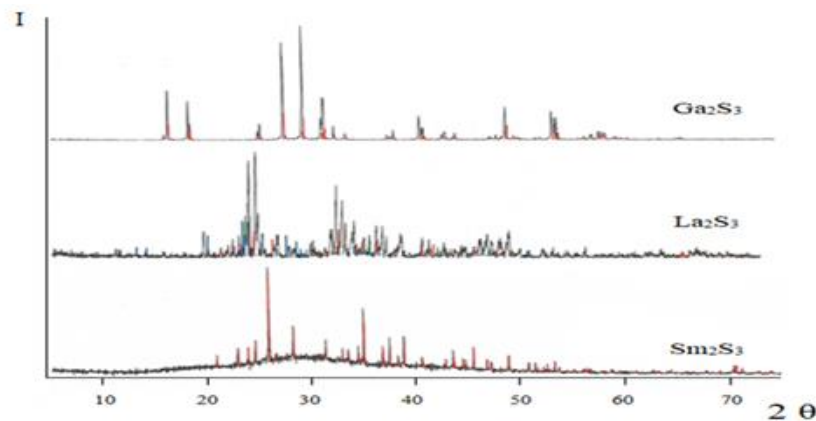


Fig. 3. X-ray diffractions of the primary components in the La_2S_3 – Ga_2S_3 – Sm_2S_3 system

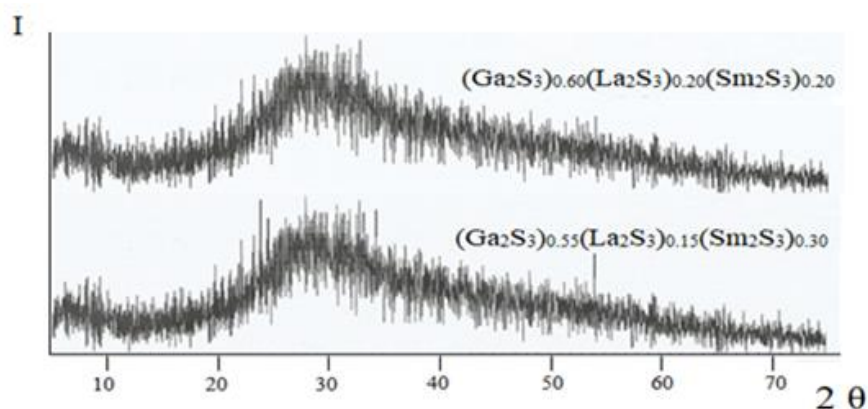


Fig. 4. X-ray diffractions of alloys the in the La_2S_3 – Ga_2S_3 – Sm_2S_3 system

The figure shows that the diffraction patterns of α - La_2S_3 and α - Sm_2S_3 used as the primary component are almost identical. However, the diffraction pattern of α - Sm_2S_3 has shifted slightly in the direction of increasing angle 2θ . On the diffraction pattern of glass with the composition $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.20}(\text{Sm}_2\text{S}_3)_{0.20}$ which corresponds to a visually transparent glass area, was not observed sharp diffraction effects. Weak diffraction bands observed in the diffractogram of glass with the composition $(\text{Ga}_2\text{S}_3)_{0.55}(\text{La}_2\text{S}_3)_{0.15}(\text{Sm}_2\text{S}_3)_{0.30}$ non-transparent glass confirm the presence of crystal centers. The crystallinity degree of the sample is 39.1%. The diffraction bands in the diffractogram of Ga_2S_3 are completely identical to the data from the International Diffraction Data Center (ICDD–00-016-0500).

It is clear from the comparison of the SEM images (fig 5) in the case of grinding of the primary components and transparent glass with the composition $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.20}(\text{Sm}_2\text{S}_3)_{0.20}$ in the La_2S_3 – Ga_2S_3 – Sm_2S_3 system that the microrelief of the transparent glass is different.

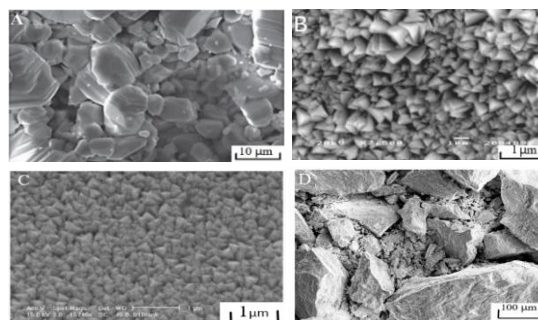


Fig. 5. SEM image of primary components and glass with the composition $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.20}(\text{Sm}_2\text{S}_3)_{0.20}$. A- Ga_2S_3 , B- La_2S_3 , C- Sm_2S_3 , D- glass with the composition $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.20}(\text{Sm}_2\text{S}_3)_{0.20}$

In figure 6 are shown the results of quantitative element analysis of glass with the composition $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.20}(\text{Sm}_2\text{S}_3)_{0.20}$ by EDX spectroscopy.

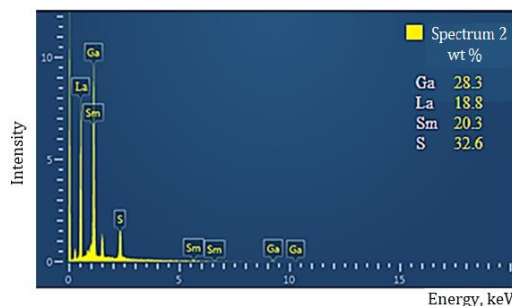


Fig. 6. Quantitative element analysis of glass with the composition $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.20}(\text{Sm}_2\text{S}_3)_{0.20}$ by EDX spectroscopy

In order to study the thermolysis of glass with the composition $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.20}(\text{Sm}_2\text{S}_3)_{0.20}$ in the La_2S_3 - Ga_2S_3 - Sm_2S_3 system, a thermogram of Differential Scanner Calorimetric (DSC) of 900 mg sample was taken in a dynamic inert (He) atmosphere (fig. 7).

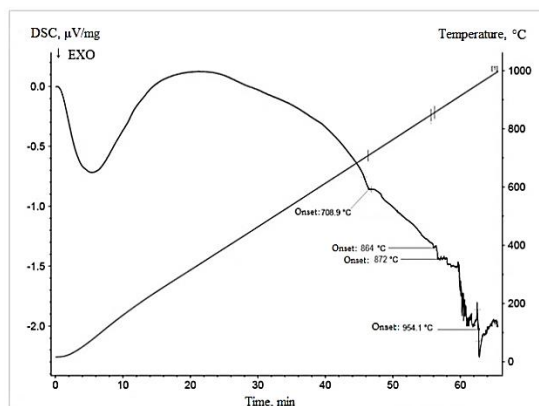


Fig. 7. DSC heating curve of glass with the composition $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.20}(\text{Sm}_2\text{S}_3)_{0.20}$ in a inert (He) atmosphere

Softening of glass with the composition $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.20}(\text{Sm}_2\text{S}_3)_{0.20}$ in an inert (He) atmosphere is $T_g=984$ K (708.9 °C) shown in figure 7. Crystallization of glass occurs at $T_c = 1139$ K (864 °C). The exo effects observed at 1147 K (872 °C) indicate the gradual disintegration of the glass. Glass with the composition $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.20}(\text{Sm}_2\text{S}_3)_{0.20}$ in an inert (He) atmosphere is thermally resistant to temperature 984 K (708.9 °C).

IR absorption spectra at 295 K of primary components ($\alpha\text{-La}_2\text{S}_3$, $\beta\text{-Ga}_2\text{S}_3$, $\alpha\text{-Sm}_2\text{S}_3$) and glass with the compositions $(\text{Ga}_2\text{S}_3)_{0.60}(\text{Sm}_2\text{S}_3)_{0.40}$, $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.20}$ in the $\text{La}_2\text{S}_3\text{-Ga}_2\text{S}_3\text{-Sm}_2\text{S}_3$ system, are given in figure 8.

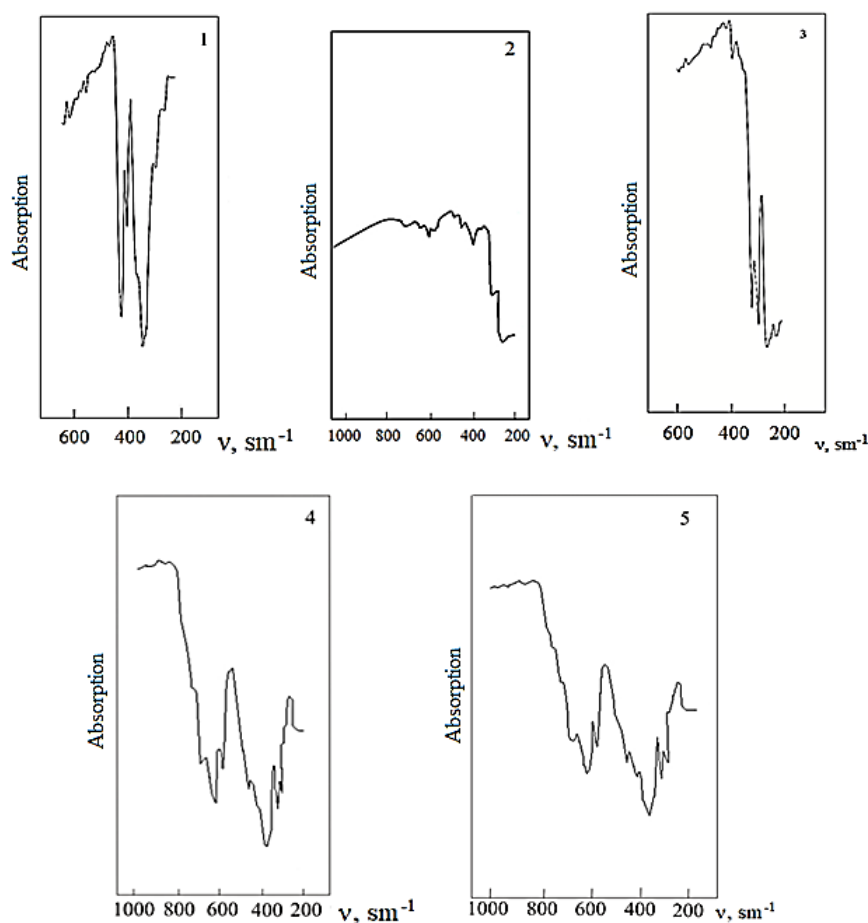


Fig. 8. IR spectrum of primary components and alloys in the $\text{La}_2\text{S}_3\text{-Ga}_2\text{S}_3\text{-Sm}_2\text{S}_3$ system: $\beta\text{-Ga}_2\text{S}_3$ (1), $\alpha\text{-Sm}_2\text{S}_3$ (2), $\alpha\text{-La}_2\text{S}_3$ (3) $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.20}(\text{Sm}_2\text{S}_3)_{0.20}$ (glass) (4), $(\text{Ga}_2\text{S}_3)_{0.60}(\text{Sm}_2\text{S}_3)_{0.40}$ (glass) (5)

As shown in figure 8 in the frequency range $220\div360$ cm^{-1} in the IR spectra of primary components ($\alpha\text{-La}_2\text{S}_3$, $\beta\text{-Ga}_2\text{S}_3$, $\alpha\text{-Sm}_2\text{S}_3$) The intense bands associated with the valence oscillations of the Me – S bonds are almost identical, whereas these bands are observed in the higher frequency range ($260\div480$ cm^{-1}) for Ga_2S_3 . In addition, a number of low-intensity bands are observed in the area of $540\div570$ cm^{-1} , which is due to the change in covalence in Me – S bonds [18].



In spectra corresponding to $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.20}(\text{Sm}_2\text{S}_3)_{0.20}$ and $(\text{Ga}_2\text{S}_3)_{0.60}(\text{Sm}_2\text{S}_3)_{0.40}$ there are peaks respectively 280 low-intensity, 320 intensive, 380 intensive and 280 low-intensity, 295 medium-intensity, 320 intensive, 360 low-intensity, 385 intensive, 420 low-intensity, 460 medium-intensity broad bands in the range of $260 \div 500 \text{ cm}^{-1}$. As can be seen, these bands move to a higher frequency range of the spectrum compared to the spectra of individual sulfides, which is probably due to the increased covalence of the Me – S bonds.

CONCLUSION

Thus, in the system $\text{La}_2\text{S}_3\text{--Ga}_2\text{S}_3\text{--Sm}_2\text{S}_3$ the boundaries of the glass formation area were determined and the thermal decomposition and IR spectra of the obtained glass were studied. It was found that glass containing $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.20}(\text{Sm}_2\text{S}_3)_{0.20}$ is resistant to atmospheric oxygen up to 865 K. The IR spectra of the obtained double and triple glasses are practically the same. Compared to the primary crystalline components, the intensities of the bands characterizing the Me – S bond in glass increase and tend to the higher frequency side of the spectrum, which is most likely due to the increase in covalence in the Me – S bond.

REFERENCES

1. Kertman, A.V. Optical sulfide ceramics // Sorosovskii Obrazov. Zh. -2000. No 6, 2, -p.93-98.
2. Minaev, V.S. Stekloobraznye poluprovodnikovye splavy (Glassy Semiconductor Alloys) / V.S.Minaev. -Moscow: Metallurgiya. -1991.
3. Gregor, R.E. Optical micro-resonators in chalcogenide glass. // Southampton: University of Southampton Faculty of Science, Engineering and Mathematics. -2009. Retrieved from. <http://eprints.soton.ac.uk>.
4. Ivanova, T.Yu. Er^{3+} to glass matrix energy transfer in Ga–Ge–S:Er³⁺ system / T.Yu.Ivanova, A.A.Man'shina, A.V.Kurochkin, [et al.] // Journal of Non-Crystalline Solids. -2002. No.298, -p.7-14
5. Bishop, S.G., Turnbull, D.A., Aitken, B.G. Excitation of rare-earth emission in chalcogenide glasses by broadband Urbach edge absorption // Journal of Non-Crystalline Solids. -2000. 266-269, p.876-883.
6. Harada, H., & Tanaka, K., Photoluminescence from Pr³⁺ doped chalcogenide glasses excited by band gap light // Journal of Non-Crystalline Solids. -1999. No.246. -p.189–196.
7. Nemec, P. Pulsed laser deposition of pure and praseodymium-doped Ge–Ga–Se amorphous chalcogenide films / P. Nemec, M.Frumar, M.Frumarova [et al.] // Optical Materials, -2000. No.15, -p.191-197.
8. Kadono, K. Upconversion luminescence of Ga₂S₃-based sulfide glasses containing Er³⁺ ions / K.Kadono, H.Higuchib, M.Takahashib [et al.] // Journal of Non-Crystalline Solids, -1995. No.184, -p.309-313.
9. Barthou, Ch., Energy transfers between Eu²⁺ and Er³⁺ in EuGa₂S₄:Er³⁺ / Ch.Barthou, P.Benalloul, B.G.Tagiyev [et al.] // Journal of Physics: Condensed Matter, -2004, No.16, -p.8075-8084.
10. Tveryanovich, Yu.S. Concentration quenching of luminescence of rare-earth ions in chalcogenide glasses // Glass Physics and Chemistry. -2003, 29 (2), –p.166-168.
11. Borisov, E.N. Deposition of Er³⁺ doped chalcogenide glass films by excimer laser ablation / E.N.Borisov, V.B.Smirnov, A.S.Tveryanovich [et al.] // Journal of Non-Crystalline Solids, -2003, 326-327, -p.316-319.
12. Bakhtiyarly, I.B. Physicochemical properties of glasses in the La₂S₃–Ga₂S₃–Nd₂S₃ system / I.B.Bakhtiyarly, A.S.Abdullayeva, A.M.Mirzoyeva [et al.] // Azerbaijan Chemical Journal, -2012, 3, -p.82-84.
13. Tsendin, K.D., Bogoslovskiy, N.A. Physics of switching and memory effects in chalcogenide glassy semiconductors // Journal of Semiconductors, -p.2012,. 46 (5), -p.559-590.



14. Turnbull, D.A., Aitken, B.G., Bishop, S.G. Broad-band excitation mechanism for photoluminescence in Er-doped $\text{Ge}_{25}\text{Ga}_{1.7}\text{As}_{8.3}\text{S}_{65}$ glasses // Journal of Non-Crystalline Solids, -1999, 244, -p.260-266.
15. Vasil'eva, A.S. Vitreous films of $\text{Ga}_{40}\text{Ge}_{17}\text{S}_{43}$ composition as a biochip substrate / A.S.Vasil'eva, E.N.Borisov, S.A.Klotchenko // Glass Physics and Chemistry, -2014, 40, 4, -p.469. Bakhtiyarlı, I.B., Abdullayeva, A.S., Mirzoyeva, A.A., Aliyev., A.B. Physicochemical properties of glasses with the compositions $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.20}(\text{Sm}_2\text{S}_3)_{0.20}$ and $(\text{Ga}_2\text{S}_3)_{0.55}(\text{La}_2\text{S}_3)_{0.15}(\text{Sm}_2\text{S}_3)_{0.30}$. // 1st Int. Chemistry and Chemical Engineering Conf., -Baku, Azerbaijan: -2013, -p.345-351.
16. Bakhtiyarov, I.B, Rustamov, P.G. System $\text{La}_2\text{S}_3\text{-La}_2\text{O}_3\text{-Ga}_2\text{S}_3$ // Journal of Inorganic Chemistry. -1987, 32, -p.1016-1021.
17. Abdullayeva, A.S., Thermal stability and IR spectrum of glass compositions $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.20}(\text{Sm}_2\text{S}_3)_{0.20}$ and $(\text{Ga}_2\text{S}_3)_{0.55}(\text{La}_2\text{S}_3)_{0.15}(\text{Sm}_2\text{S}_3)_{0.30}$ // Scientific journal "Young scientist". Rubric "Chemistry", -2019, (278). 40 –p. 4-8.

$\text{La}_2\text{S}_3\text{-Ga}_2\text{S}_3\text{-Sm}_2\text{S}_3$ SİSTEMİNDƏ SİNTEZ VƏ ŞÜŞƏ ƏMƏLƏGƏLMƏNİN TƏDQIQI

A.S. Abdullayeva

$\text{La}_2\text{S}_3\text{-Ga}_2\text{S}_3\text{-Sm}_2\text{S}_3$ sistemində şüşə əmələgəlmə sahəsinin sərhədləri eyni vaxtda termiki analiz, rentgen faza analizi və mikrorentgenspektral analiz metodlarından istifadə etməklə müəyyən edilmişdir. $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.20}(\text{Sm}_2\text{S}_3)_{0.20}$ və $(\text{Ga}_2\text{S}_3)_{0.55}(\text{La}_2\text{S}_3)_{0.15}(\text{Sm}_2\text{S}_3)_{0.30}$ tərkibli şüşələrin fiziki-kimyəvi xassələri və termal parçalanması, həmçinin İQ spektri öyrənilmişdir. Müəyyən edilmişdir ki, 865 K-də $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.20}(\text{Sm}_2\text{S}_3)_{0.20}$ tərkibli şüşə ətraf mühitin oksigeninə qarşı davamlıdır. Me-S rabitəsini xarakterizə edən şüşə zolaqlarının İQ spektrində kristal ilkin komponentlərlə müqayisədə intensivlik artır və spektrin yüksək tezlikli tərəfinə keçir, bu, ehtimal ki, Me-S rabitəsinin kovalentliyinin artması ilə əlaqədardır.

Açar sözlər: fiziki-kimyəvi xassələr, İQ-spektr, termiki parçalanma, xalkogenidlər, lantanoidlər

ИССЛЕДОВАНИЕ СИНТЕЗА И СТЕКЛООБРАЗОВАНИЯ В СИСТЕМЕ $\text{La}_2\text{S}_3\text{-Ga}_2\text{S}_3\text{-Sm}_2\text{S}_3$

А.С. Абдуллаева

Границы области стеклообразования в системе $\text{La}_2\text{S}_3\text{-Ga}_2\text{S}_3\text{-Sm}_2\text{S}_3$ определяли одновременно методами термического анализа, рентгенофазового анализа и микро рентгено-спектрального анализа. Исследованы физико-химические свойства и термическое разложение стекол, содержащих $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.20}(\text{Sm}_2\text{S}_3)_{0.20}$ и $(\text{Ga}_2\text{S}_3)_{0.55}(\text{La}_2\text{S}_3)_{0.15}(\text{Sm}_2\text{S}_3)_{0.30}$, а также ИК-спектр. Было определено, что стекло, содержащее $(\text{Ga}_2\text{S}_3)_{0.60}(\text{La}_2\text{S}_3)_{0.20}(\text{Sm}_2\text{S}_3)_{0.20}$ при 865 К, устойчиво к кислороду окружающей среды. В ИК-спектре полос стекла, характеризующих связь Me-S, увеличивается интенсивность по сравнению с кристаллическими первичными компонентами и смещается в высокочастотную сторону спектра, что, вероятно, связано с увеличением ковалентности связи Me-S связь.

Ключевые слова: физико-химические свойства, ИК-спектр, термическое разложение, халькогениды, лантаноиды