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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

PURPOSE SYNTHESIS AND PROPERTIES OF OPTICALLY SENSITIVE SULPHIDE GLASSES LANTHANIDE MIXED CATIONIC WITH GALLIUM

Speciality: 2303.01 – Inorganic chemistry

Field of science: Chemistry

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Baku-2023

The work was performed at Laboratory "Chalcogenides of transition elements" of the Institute of Catalysis and Inorganic Chemistry named after academician M. Nagiyev of Ministry of Science and Education Republic of Azerbaijan

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GENERAL CHARACTERISTICS OF WORK

The actuality of the subject and the degree of development. Semiconducting chalcogenide glasses have several unique properties that are poorly observed (or not at all) in crystals. Thus, these glasses are superior due to radiation exposure, resistance to the effects of additives, over-extrusion effect (эффект переключения) due to the change of "photostructure", memory properties and simple synthesis technology. Because of these properties, semiconducting chalcogenide glasses are used on an industrial scale in microelectronics - in the production of black-and-white and color video tapes, electrographic coatings, photo-, electronic- and X-ray resistors, memory elements of electrical switches and optical parts for infrared optics ([1, 2]) In addition, chalcogenide glasses are of great importance in the development of fiber lasers, amplifiers and the development of disks with a storage capacity of more than a billion bytes ([3]).

Although Ga_2S_3 does not form glass individually, it has the ability of an effective glass-forming matrix during chemical interaction with oxides, oxysulfides, oxyfluorides and sulfides of lanthanides and ensures equal distribution of the activator such as Lewis acid in the volume of the glass. İlluminator lanthanide ions (activator) as an solves in the matrix create an illumination center with a high-intensity radiation transition in a wide spectrum range. The value of

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[1] Lini, L. Structural characterization and compositional dependence of the optical properties of Ge–Ga–La–S chalcohalide glass system ⁄ Qing Jiao, Changgui Lin, Shixun Dai [et al.] // Optical Materials, – 2018. 78. –p. 295-301.

[2] El Naggar, A.M. Exploration of Nonlinear Optical Features of Ga_2S_3-La_2S_3 Glasses for Optoelectronic Applications ⁄ A.A. Albassam, G. Lakshminarayana, V.V. Halyan [et al.] // Glass Physics and Chemistry, –2019. 45. –p. 467–471.

[3] Yang, A. Dy^{3+}- doped Ga_2S_3-Sb_2S_3-La_2S_3 chalcogenide glass for mid-infrared fiber laser medium ⁄ M. Sun, H. Ren, H.Lin [et al.] // Journal of Luminescence, – 2021. 237 , art. no. 118169.

the emitted quantum determines the spectral domain of the illumination.

Since the illumination spectra of lanthanoid ions participating as activators in glasses have a linear structure, the width of the main band
in illumination is 1-2 nm, which means high monochromatic radiation.

The presence of Er^{3+} ion as an activator in various matrices is known in the literature. However, the oscillator strength of Er^{3+} ion transitions is relatively weak and gives a narrow emission ([4]). It should be noted that using the Eu^{2+} ion as a sensitizer, it is possible to obtain more effective luminophores by enhancing the energy transfer to the activator (Er^{3+} ion).

Passive lanthanide ions in the matrix also play a role in this effect. However, the formation of crystal centers in the system of compounds that can be obtained by chemical interaction of gallium and lanthanide sulfides ($LnGaS_3$, $Ln_6Ga_{10/3}S_{14}$, even $La_{10/3}Ga_6S_{14}$, which are not observed in the state diagram at chemical equilibrium) deteriorates the optical properties of glass. In order to eliminate this shortcoming in the thesis work, not only the nature of lanthanoids used as activators, but also the nature of matrices is planned to be studied in parallel. Therefore, the topic of the dissertation devoted to the synthesis of sulfide glasses of lanthanides, the study of the physico-chemical and optical properties of the obtained new phases is relevant from a scientific and practical point of view.

Object and subject of research. As the research object of the dissertation, were determined the cationic sulfide glasses of lanthanides mixed with gallium, and were selected as the subject samples from the area of glass formation in La_2S_3-Ga_2S_3-$Ln_2'S_3$

[4] Halyan, V.V. Specific features of Stokes photoluminescence of the La_2S_3–Ga_2S_3–$E_{r2}S_3$ glasses / V.O. Yukhymchuk, Ye.G. Gule, I.V. Kityk [et al.] // Optical Materials, –2022. 128, –p. 112394

(Ln'= Nd, Sm, Er) and Ln_2S_3-Ga_2S_3-EuS (Ln = La, Nd, Sm, Er), quasi-ternary systems.

The purpose and responsibilities of the study. It consists in determining the boundaries of the glass formation area in quasi-ternary systems La_2S_3-Ga_2S_3-$Ln_2'S_3$ (Ln'= Nd, Sm, Er) and Ln_2S_3-Ga_2S_3-EuS (Ln =La, Nd, Sm, Er), separating practically suitable compositions,

studying their physico-chemical and luminescence properties and giving recommendations on their application.

To achieve the purpose of the research work, next issues have been resolved:

- to determine the boundaries of the glass formation area in La_2S_3-Ga_2S_3-$Ln_2'S_3$ (Ln'= Nd, Sm, Er) və Ln_2S_3-Ga_2S_3-EuS (Ln = La, Nd, Sm, Er) quasi-ternary systems;
- to study the thermolysis of samples from the area of glass formation in air, in an inert environment (He) and their relationship to solvents;
- to study the physicochemical, spectral and luminescence properties of glass and make recommendations on their practical application.

Methods of research. Samples synthesized in stoichiometric composition were studied by complex methods of physicochemical analysis - - differential thermal analysis (DTA), differential thermal gravimetric analysis (DTGA), X-ray phase analysis (RFA), micro-X-ray spectral analysis (SEM, REM, EDX), measurement of IR spectrum, density and luminescence properties.

Defensive provisions:

- Determination of the area of glass formation in La_2S_3-Ga_2S_3-$Ln_2'S_3$ (Ln'= Nd, Sm, Er) and Ln_2S_3-Ga_2S_3-EuS (Ln = La, Nd, Sm, Er) quasi-ternary systems and experimental results on the conditions of synthesis.
- Dependence of glass formation on the load of lanthanide nucleus in quasi-ternary systems, temperature of sulfide glass in the atmosphere and inert conditions, resistance to oxidizing reagents and solvents.

- Experimental results set of studies of photoluminescence properties of $(Er_2S_3)_{0.05}(Ga_2S_3)_{0.80}(EuS)_{0.15}$ and $(La_2S_3)_{0.25}(Ga_2S_3)_{0.70}(Nd_2S_3)_{0.05}$ composite glasses.
- Recommendations on the application of synthesized glasses.

Scientific novelty of the research.

- The boundaries of the glass formation areas under sulfur pressure in La_2S_3-Ga_2S_3-$Ln_2'S_3$ (Ln′= Nd, Sm, Er) and Ln_2S_3-Ga_2S_3-EuS (Ln = La, Nd, Sm, Er) quasi-ternary systems have been clarified.
- found that in Ga_2S_3-Ln_2S_3 quasi-binary systems, which form the sides of a quasi-ternary system, glass formation decreases as the load on the lanthanide nucleus increases, and finally Er_2S_3 does not form glass directly with Ga_2S_3 in our study.
- the thermolysis of glass shows that they are oxidized in air by stepwise reactions after softening (T_g) and crystallization (T_c) temperatures, and decompose in an inert medium.
- IR spectral analysis of samples from the glass area compared to the corresponding crystals shows that the covalence is higher in glass than in crystalline samples.
- studied the $(Ga_2S_3)_{0.70}(La_2S_3)_{0.25}(Nd_2S_3)_{0.05}$ glass sample shows a laser property at a wavelength of 1.08 μm at room temperature. The weak laser properties of the Nd^{3+} ion in these glasses compared to the corresponding crystal matrices are due to the relatively high beam loss in the glass. However, it is possible to improve the quality of the laser in these glasses due to the optimal density of the activator and the minimum length.
- Since Er_2S_3 does not form a glass area with Ga_2S_3, it is replaced by $(Ga_2S_3)_{1-x}(EuS)_x$ glass area and the photoluminescence spectrum of a $(Ga_2S_3)_{0.80}(EuS)_{0.15}(Er_2S_3)_{0.05}$ sample which excited with a 337.1 nm wavelength “Laser Photonics LN 1000” nitrogen laser has been studied at 300 K temperature.
- The Eu^{2+} ion used as a sensitizer when the $(Ga_2S_3)_{0.80}(EuS)_{0.15}(Er_2S_3)_{0.05}$ glass is irradiated with an IR laser enhances the transfer of energy to the Er^{3+} ion. Light is converted from the IR field to the visible field, ie antstox luminescence is observed.

Theoretical and practical significance of the research.

The synthesis conditions of sulfide glass in the studied systems can be used to solve similar technological problems. They can also be included in relevant books, databases and international scientific information systems as new scientific indicators.

Approbation and application.

The results of scientific work were discussed at the following scientific conferences:

1. Ümummilli Lider H.Əliyevin anadan olmasının 90 illiyinə həsr olunmuş 1-ci beynəlxalq Kimya və Kimya mühəndisliyi konfransı, Bakı, Azərbaycan. 2013;
2. Akad. M.F.Nağıyevin 105 illiyinə həsr olunmuş elmi konfrans, Bakı, Azərbaycan. 2013;
3. Gənc alim və mütəxəssislərin 1-ci beynəlxalq elmi konfransı, Bakı, Azərbaycan. 2014;
4. Международная научная конференция «Полифункциональные химические материалы и технологии», Томск, Россия. 2015;
5. XIX Международная конференция «Физика прочности и пластичности материалов», Самара, Россия. 2015;
6. Akad. Toğrul Şaxtaxtinskinin 90 illik yubileyinə həsr olunmuş respublika elmi konfransı, Bakı, Azərbaycan. 2015;
7. "AMEA-70 Akademik Elm Həftəliyi-2015" Beynəlxalq Multidissiplinar Forumu, Bakı, Azərbaycan. 2015;
8. AMEA-nın akad. M.F.Nağıyev adına Kataliz və Qeyri-üzvi Kimya İnstitutunun 80 illiyinə həsr olunmuş elmi konfransı, Bakı, Azərbaycan. 2016;
9. Ümummilli Lider H.Əliyevin anadan olmasının 95-ci ildönümünə həsr olunmuş doktorant, magistr və tədqiqatçıların XII Beynəlxalq Elmi Konfransı, "Kimyanın aktual problemləri", Bakı, Azərbaycan. 2018;
10. Ümummilli Lider H.Əliyevin anadan olmasının 96-cı ildönümünə həsr olunmuş doktorant, magistr və tədqiqatçıların XIII Beynəlxalq Elmi Konfransı, "Kimyanın aktual problemləri", Bakı, Azərbaycan. 2019;

11. XXIX Российском молодежной научной конференции с международным участием, посвященной 150-летию Периодической таблицы химических элементов, «Проблема теоретической и экспериментальной химии», Екатеринбург, Россия. 2019;
12. Proceedings of republican scientific-practical conference on “Problems of modern chemistry and development trends”, Baku, Azerbaijan. 2020;
13. Ümummilli Lider H.Əliyevin anadan olmasının 99-cu ildönümünə həsr olunmuş Beynəlxalq Elmi Konfrans, “Müasir təbiət və iqtisad elmlərinin aktual problemləri”, Gəncə, Azərbaycan. 2022.

The $(Ga_2S_3)_{0.70}(La_2S_3)_{0.25}(Nd_2S_3)_{0.05}$ glass can be used as a laser material in the manufacture of 1.3 micron wavelength amplifiers for telecommunications in fiber-optic communication systems.

The $(Ga_2S_3)_{0.80}(EuS)_{0.15}(Er_2S_3)_{0.05}$ glass can be used in night vision devices such as antistox phosphors and fiber-optic communication systems.

21 scientific papers were published on the main results of research work on the topic of the dissertation. 8 of them are articles and 13 are theses. 3 of the articles were published in the periodicals "Inorganic Material", "Journal of Inorganic Chemistry" and "Physics and Chemistry of Glass" which are included in the international summarization and indexing systems of the Russian Academy of Sciences. In particular, three of the articles are unco-authored.

Name of the organization where the dissertation work is carried out. The dissertation work was carried out at the Institute of Catalysis and Inorganic Chemistry named after Academician M. Nagiyev of the Ministry of Science and Education in accordance with the topics of the research plan (Subject 2) "Physico-chemical and thermodynamic bases of obtaining materials with functional properties based on lanthanide compounds" (State registration no. 0111 Az 2111 2011-2016 years) and "Improving the methods of obtaining low-tonnage and unique inorganic materials important for high technologies, developing methods of corrosion protection of hirtotechnical facilities, giving recommendations for application" (State registration No. 0115 Az 2100 2015 -2020 years).

The structure and scope of the dissertation. The dissertation consists of an introduction (13327 signs), 4 chapters (Chapter I 53981 signs, Chapter II 25481 signs, Chapter III 57671 signs, Chapter IV 8082 signs), results (2693 signs) and a list of 248 references. The dissertation work, including 7 tables and 78 figures, is 151 (161235 one hundred and sixty one thousand two hundred and thirty five signs)

computer printed sheets.

The author is responsible for formulating the purpose of the dissertation, developing a methodological approach to its solution, performing most of the experimental research, interpreting the results and presenting them to the press.

MAIN CONTENT OF THE WORK

In the **introduction** of the dissertation (8 p.) The relevance of the topic is substantiated, the degree of development is clarified, the purpose of the work, issues to be solved, scientific innovations, theoretical and practical significance, main provisions, the degree of publication of the results, recommended areas of application and individual chapters. reflected in the brief content.

The first chapter is a literary review (40 p.). It examines modern ideas about the formation of glass, the degree of development of lanthanides, cationic sulfide glass mixed with gallium - the synthesis, physical and chemical properties, selection of matrices and activators, and applications of these glass.

In the second chapter (17 p.) Required for the study of glass formation areas in quasi-triangular systems La_2S_3-Ga_2S_3-$Ln_2'S_3$ (Ln ′ = Nd, Sm, Er) and Ln_2S_3-Ga_2S_3-EuS (Ln = La, Nd, Sm, Er) A brief description of the components, synthesis of alloys and research methods are given.

Thus, glass alloys consisting of primary components were synthesized in a special reactor at a temperature of 1425 K for 2.5

hours under the pressure of sulfur and immersed in water at room temperature and rapidly cooled (υ = 100 deg/m).

DTA is defined in STA449F3 Jupiter (NETZSCH, Germany) synchronous thermal analyzer, DTQA is defined in Q-1500D (MOM, Hungary) derivatograph, RFA is defined in D2 Phaser (Bruker, Germany) automatic diffractometer, REM is defined in and EDX Sigma VP Scanning Electron Microscope (Carle Zeiss) used in the research , Germany) and the density was determined by pycnometric method (toluene as a filler). The IR spectra of the glass and primary components under study were recorded on a Specord M80 spectrometer at 295 K at a wavelength of 200-3000 cm^{-1}. The luminescence spectrum was taken on an SDL-1 industrial device, and the samples were excited with an LMP-11 He-Cd laser.

In the third chapter (56 p.) La_2S_3-Ga_2S_3-$Ln_2'S_3$ (Ln ′ = Nd, Sm, Er) [2, 12, 16] and Ln_2S_3-Ga_2S_3-EuS (Ln = La, Nd, Sm, Er) [8 , 9, 10, 15, 19, 20] The results of the study of the physical and chemical properties of the new phases and the determination of the areas of glass formation in quasi-ternary systems (figure 1).

The areas of dark colored visual transparent glass formation shown in figure1 are bounded on both sides by a hatched strip, which characterizes the area of opaque glass with crystal centers.

Given the volume of the abstract and the similarity of the nature of the glass formation, we need to comment in more detail on the three most important systems in practice - La_2S_3-Ga_2S_3-Nd_2S_3, La_2S_3-Ga_2S_3-Er_2S_3 and Nd_2S_3-Ga_2S_3-EuS.

In the quasi-ternary system La_2S_3-Ga_2S_3-Nd_2S_3 [1,7,17] to define the boundaries of the glass formation area (Figure 1a) 45 samples prepared from stoichiometric quantities of primary components (β-Ga_2S_3, α-La_2S_3 and α-Nd_2S_3) were synthesized by the method shown in Chapter II. 9 samples of them belong to the Ga_2S_3-Nd_2S_3 system, 6 to the Ga_2S_3-Nd_2S_3 quasibinar system, and other samples belong to the La_2S_3-Ga_2S_3-Nd_2S_3 quasi-ternary system.

The color of the glass corresponding to the Ga_2S_3-La_2S_3 concentration plane depends on the amount of La_2S_3 and the thickness of the sample. Thus, as the amount of La_2S_3 increases, the color of the sample darkens. The sample is yellow in thin thickness and amber in thickness. On the Ga_2S_3-Nd_2S_3 side, depending on the concentration of Nd_2S_3, the color changes from light lilac to purple.

In the triple composition of the glass formation area, the color changes from light jasmine to dark gray as the concentration of Nd_2S_3 increases (Fig. 2).

Glass containing $(Ga_2S_3)_{1-x}(La_2S_3)_{x-y}(Nd_2S_3)_y$ at room temperature resistant to air, slightly hydrolyzed when left in water, partially decomposed by alkali and mineral acids, completely soluble in chromium mixture when heated.

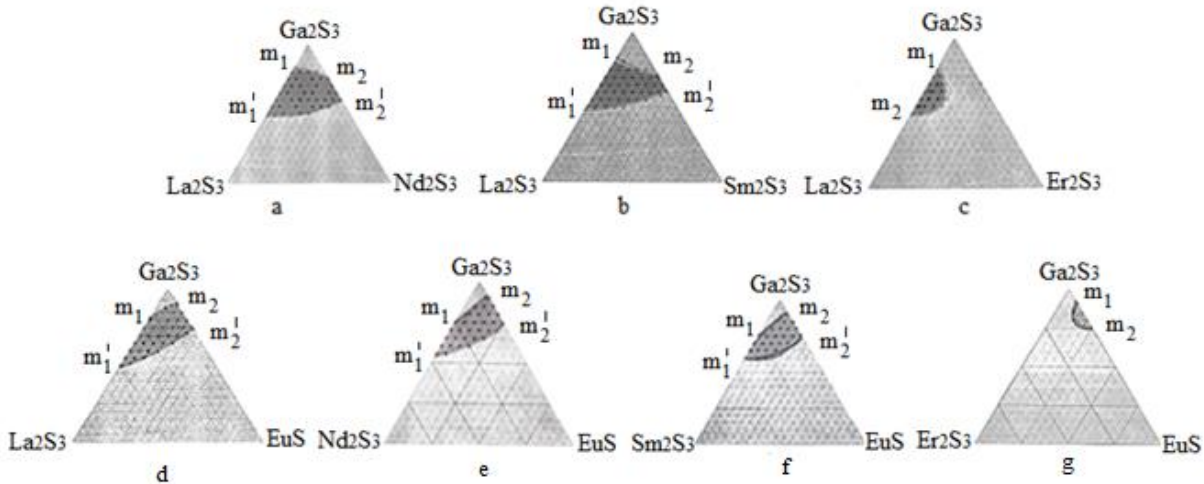

Figure 1. Dependence of the composition of the glass formation areas in quasi-ternary systems La_2S_3-Ga_2S_3-$Ln_2'S_3$ (Ln′=Nd, Sm, Er) and Ln_2S_3-Ga_2S_3-EuS (Ln=La, Nd, Sm, Er)

Figure 2. Photo of glass containing $(Ga_2S_3)_{0.70}(La_2S_3)_{0.25}(Nd_2S_3)_{0.05}$ from the La_2S_3-Ga_2S_3-Nd_2S_3 quasi-ternary system

Density of ternary glasses from the Ga_2S_3-La_2S_3-Nd_2S_3 system $(Ga_2S_3)_{0.65}(La_2S_3)_{0.30}(Nd_2S_3)_{0.05}$; $(Ga_2S_3)_{0.65}(La_2S_3)_{0.25}(Nd_2S_3)_{0.10}$; $(Ga_2S_3)_{0.65}(La_2S_3)_{0.20}(Nd_2S_3)_{0.15}$; $(Ga_2S_3)_{0.65}(La_2S_3)_{0.15}(Nd_2S_3)_{0.20}$; $(Ga_2S_3)_{0.65}(La_2S_3)_{0.10}(Nd_2S_3)_{0.25}$; $(Ga_2S_3)_{0.65}(La_2S_3)_{0.05}(Nd_2S_3)_{0.30}$ are respectively 4.0109, 4.0277, 4.0361, 4.0448, 4.0533 və 4.0619 g/cm^3.

The boundaries of the glass formation area in the quasi-ternary system La_2S_3-Ga_2S_3-Nd_2S_3 are based on physical and chemical analysis - XRD, XRM, EDX, DTA, TGA methods (Fig. 1 (a), m_1 m_2 m_1' m_2' area). On the sides of the ternary system (La_2S_3-Ga_2S_3, Nd_2S_3-Ga_2S_3), it is once again confirmed that glass formation ([5, 6]) occurs around corresponding nonvariant eutectic equilibrium points.
Glass formation observed in the Ga_2S_3-La_2S_3 system (m_1m_1') in the 17÷52 mol.% La_2S_3 (transparent glass 20÷50 mol.% La_2S_3) concentration range, while in the Ga_2S_3-Nd_2S_3 system in the 24÷41 mol.% Nd_2S_3 (m_2m_2') (transparent glass 25÷40 mol.% Nd_2S_3) concentration range (figure 1 (a)). Figure 3 shows the diffractograms of the primary components and the glass alloys. Compatible with the appropriate crystallographic readings ([7]) of the primary components.

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[5] Алиева, О.М., Алиева, О.А., Рустамов, П.Г., Взаимодействие в системах Nd_2S_3-Ga_2S_3, Sm_2S_3-Ga_2S_3 и $Nd_6Ga_{10/3}S_{14}$–$Sm_6Ga_{10/3}S_{14}$ // Журнал Неорганической Матреалы, –1987, т.23, №1, с.22-24.

[6] Бахтияров, И.Б., Рустамов, П.Г. Система La_2S_3-La_2O_3-Ga_2S_3 Журнал Неорганической Химии. –1987. т. 32. –с. 1016-1021.

[7] International Centre for Diffraction Data. ICDD. PDF. –2011.

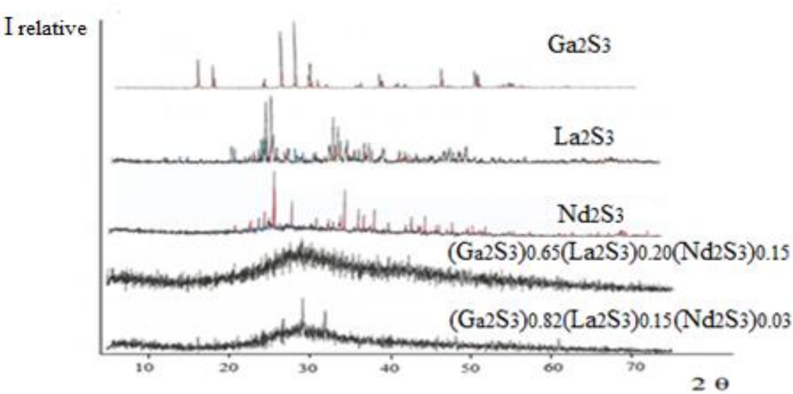


Figure 3. Diffractograms of primary components and alloys in the La_2S_3-Ga_2S_3-Nd_2S_3 quasi-ternary system

Figure 4 shows the initial components of the La_2S_3-Ga_2S_3-Nd_2S_3 quasi-teernary system and a transparent glass (in the case of abrasion) containing $(Ga_2S_3)_{0.65}(La_2S_3)_{0.20}(Nd_2S_3)_{0.15}$ under a Scanning Electron Microscope. A comparative analysis of the images obtained shows that the microrelief of transparent glass is completely different from the original components.

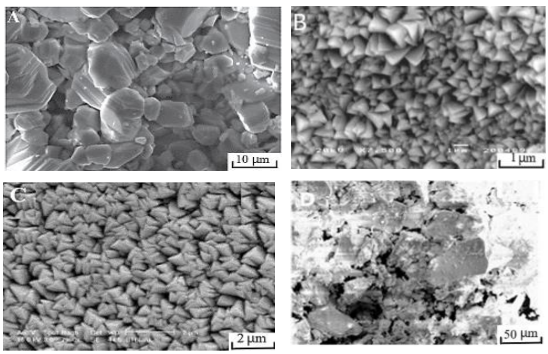


Figure 4. Description of primary components and $(Ga_2S_3)_{0.65}(La_2S_3)_{0.20}(Nd_2S_3)_{0.15}$ containing glass on a Scanning Electron Microscope. A-Ga_2S_3, B-La_2S_3, C-Nd_2S_3, D-$(Ga_2S_3)_{0.65}(La_2S_3)_{0.20}(Nd_2S_3)_{0.15}$ containing glass

Figure 5 shows the results of elemental analysis of the amount of transparent glass containing $(Ga_2S_3)_{0.65}(La_2S_3)_{0.20}(Nd_2S_3)_{0.15}$ by EDX method.

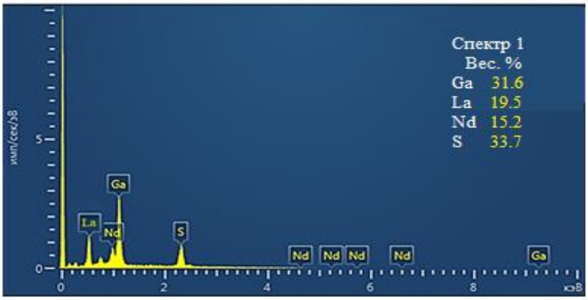


Figure 5. Quantitative element analysis of $(Ga_2S_3)_{0.65}(La_2S_3)_{0.20}(Nd_2S_3)_{0.15}$ glass

The results of the analysis correspond to the stoichiometric composition of the glass.

To study the thermal stability of the sample drawn Derivatogram in dynamic air and Differential Scanning Calorimetric (DSC) thermogram of transparent glass containing $(Ga_2S_3)_{0.65}(La_2S_3)_{0.20}(Nd_2S_3)_{0.15}$ in inert (He) medium (figure 6 and 7).

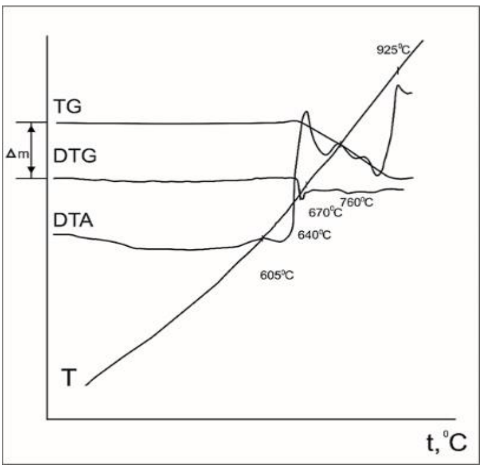


Figure 6. Derivatogram in air of

$(Ga_2S_3)_{0.65}(La_2S_3)_{0.20}(Nd_2S_3)_{0.15}$ glass

It is clear from figure 8 that $(Ga_2S_3)_{0.65}(La_2S_3)_{0.20}(Nd_2S_3)_{0.15}$ containing glass at 880 K temperature melts with endoeffect. (T_g=880 K). Because the exo effects observed in the range of 915÷ 1200 K correspond to the area of mass loss (TG) we explain these effects by the gradual oxidation of glass by oxygen in the air.

Mass loss: $\Delta m = \frac{m_1 - m_2}{m_1} \cdot 100\ \% = \frac{200-182}{200} \cdot 100\ \% = 9\ \%$

The absence of glass crystallization temperature (T_c) seems to be due to its proximity to the oxidation temperature. It was determined by the method of synchronous thermal analysis (STA) that (figure 7) the softening of the glass containing $(Ga_2S_3)_{0.65}(La_2S_3)_{0.20}(Nd_2S_3)_{0.15}$ occurs at T_g=1003 K (728.5 °C) temperature, in contrast to the derivatogram taken in air. The crystallization temperature corresponds to T_c=1139K (864.5°C). So heat resistance of $(Ga_2S_3)_{0.65}(La_2S_3)_{0.20}(Nd_2S_3)_{0.15}$ containing glass in an inert (He) environment ~1000 K.

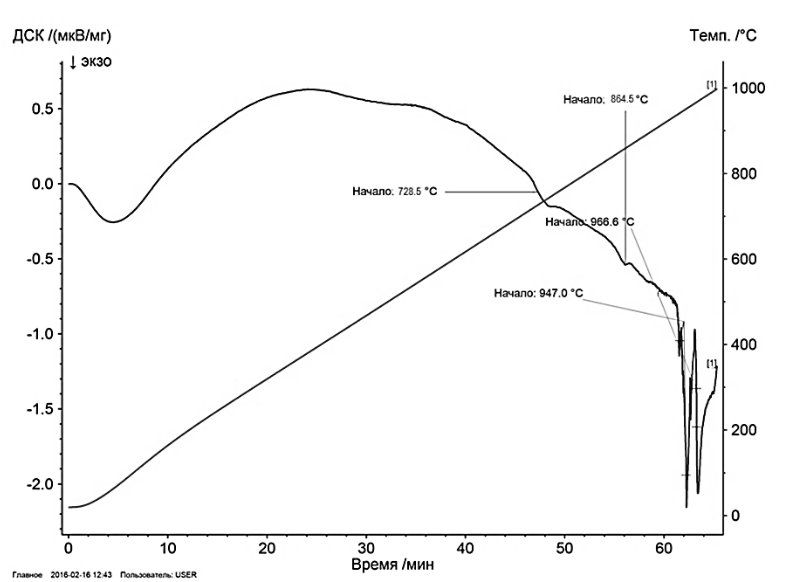


Figure 7. Differential Scanning Calorimetric (DSC) thermogram

of $(Ga_2S_3)_{0.65}(La_2S_3)_{0.20}(Nd_2S_3)_{0.15}$ glass in inert (He) medium

IR absorption spectra of primary components (α-La_2S_3, β-Ga_2S_3 and α-Nd_2S_3) and $(Ga_2S_3)_{0.65}(La_2S_3)_{0.20}(Nd_2S_3)_{0.15}$ (transparent), $(Ga_2S_3)_{0.82}(La_2S_3)_{0.15}(Nd_2S_3)_{0.03}$ (non-transparent) containing glasses in the La_2S_3-Ga_2S_3-Nd_2S_3 system at 300 K temperature are shown in figure 8.

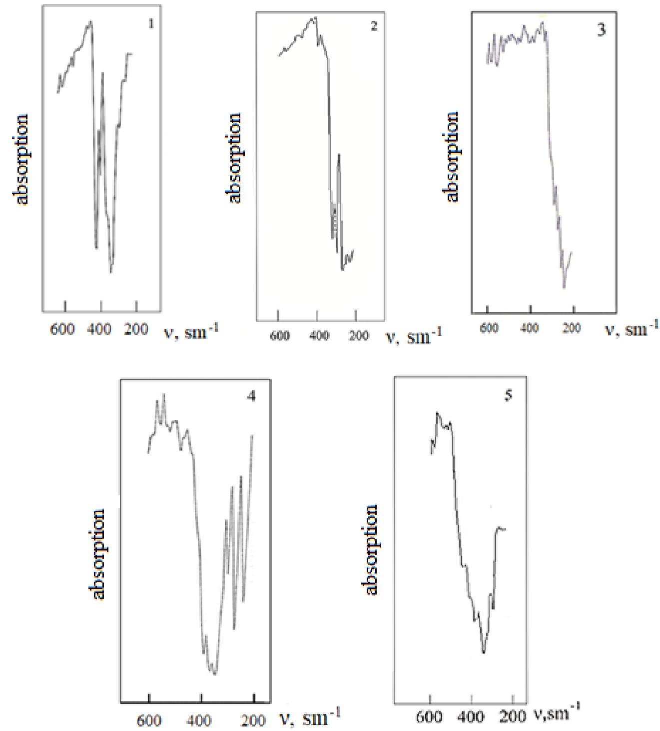


Figure 8. IR spectra of primary components and alloys in La_2S_3-Ga_2S_3-Nd_2S_3 quasi-ternary system: β-Ga_2S_3 (1), α-La_2S_3 (2), Nd_2S_3 (3) $(Ga_2S_3)_{0.65}(La_2S_3)_{0.20}(Nd_2S_3)_{0.15}$ (4), $(Ga_2S_3)_{0.82}(La_2S_3)_{0.15}(Nd_2S_3)_{0.03}$ (5)

As you can see in the figure for α-La_2S_3 and α-Nd_2S_3 compounds in 220÷360 cm^{-1} wavelength The intense bands that characterize the valence oscillations in the Me−S bond are almost identical. However, in the identical β-Ga_2S_3 compound, the bands characterizing the valence oscillations of the Ga−S bond are observed in the higher frequency range of the spectrum (260÷480 cm^{-1}). In addition, several weak bands observed in the wavelength of sulfides (540÷750 cm^{-1}) in the spectrum, in our opinion, characterize the valence oscillations of the Me−S bond. It should be noted that these streaks observed in both of these components are more intense. Compared to the primary components the bands that characterize the Me−S bond slip of the spectrum into the high frequency field reaffirms the increase in covalence in glass.

The Ga_2S_3-Er_2S_3 side of the **La_2S_3-Ga_2S_3-Er_2S_3** system [4, 11, 18] was studied first by French scientists in the crystalline phase and a phase diagram was constructed. ([8]).

It was revealed that, with a peripheral reaction in the system ($m+Er_2S_3 \rightarrow Er_3GaS_6$) only Er_3GaS_6 compound is formed wich melts incongruent. The authors did not observe the formation of glass in the Ga_2S_3-Er_2S_3 system and in our study, this result was reaffirmed. However, the authors of the ([9]) study noted that when the sharp cooling temperature is 1475 K, a glass with only one concentration - $(Ga_2S_3)_{0.50}(Er_2S_3)_{0.50}$ is formed.

Before ([10]), the authors studied the area of glass formation in the La_2S_3-Ga_2S_3-Er_2S_3 quasi-ternary system with a sharp cooling temperature of 1375 K and determined its dependence on the hardness (figure 1 (c)).

[8] Loireau-Lozac'h, A.M., Guittard, M., Flahaut, J. Systemes L_2S_3–Ga_2S_3 (L=La, Ce, Dy, Er et Y) Diagrammes de phases // Materials Research Bulletin. – 1977. v.12, –p. 881-886.

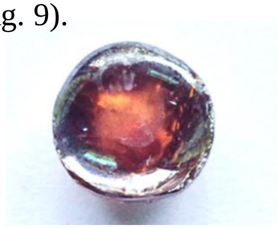
[9] Loireau-Lozac'h, A.M., Guittard, M. et Flahaut, J. Verres formes par les sulfures L_2S_3 des terres rares avec le sulfure de gallium Ga_2S_3 // Materials Research Bulletin. – 1976. v. 11, – p. 148.

[10] Bakhtiyarly, I.B., Asadly, L.Sh. Mirzoeva, A.A. Synthesis and physicochemical properties of glasses in La_2S_3-Ga_2S_3-Er_2S_3 system // Azerbaijan Chemical Journal –2008, no.1, –p. 131–134.

Later, the authors of ([11]) studied the IR and luminescent properties of several samples in the concentration range shown in figure 1 (c).

However, unfortunately, the authors did not refer to the work published long before them ([6]) continuing our previous research, we synthesized 26 samples composed of stoichiometric initial components (β-Ga_2S_3, α-La_2S_3 and δ-Er_2S_3) in the La_2S_3-Ga_2S_3-Er_2S_3 quasi-ternary system, starting from the Ga_2S_3-La_2S_3 concentration plane [18]. 7 of them fall into the solid plane of the quasibinar system Ga_2S_3-La_2S_3 ([2]), [18]. Synthesis of the samples was carried out in 2.5 hours at a temperature of 1425 K in a “steclographite” powder placed in a quartz reactor under sulfur pressure, as shown in the previous quasi-ternary system. The rapidly cooling process was completed by immersing the reactor from the synthesis temperature to room temperature water.

As can be seen from figure 1 (c), in the La_2S_3-Ga_2S_3-Er_2S_3 quasi-ternary system, the glass formation area increases depending on the amount of Er_2S_3, starting from the density (m_1m_2) around the nonvariant point (e) in the La_2S_3-Ga_2S_3 concentration plane. The dark area that characterizes the visually transparent glass is bounded by a limited strip of opaque glass. The visual opacity of the glass is due to the formation of crystal centers in the composition. In the La_2S_3-Ga_2S_3-Er_2S_3 quasi-ternary system, the color of the alloys falling on the glass area varies from yellow to brown depending on the amount of Er_2S_3, starting from yellow in the Ga_2S_3-La_2S_3 concentration plane (fig. 9).



[11] Kityk, I.V., Halyan, V.V., Yukhymchuk, V.O. NIR and visible luminescence features of erbium doped Ga_2S_3–La_2S_3 glasses // Journal of Non-Crystalline Solids. – 2018. v. 498. – p. 380-385.

Figure 9. Photo description of the $(Ga_2S_3)_{0.60}(La_2S_3)_{0.35}(Er_2S_3)_{0.05}$ glass in the La_2S_3-Ga_2S_3-Er_2S_3 quasi-ternary system

The samples synthesized from the glass formation area are resistant to air, water and organic solvents at room temperature. Decomposes partially under the influence of alkaline and mineral acids (smells of hydrogen sulfide). When heated, it dissolves in the "chromium mixture". The density of the $(Ga_2S_3)_{0.60}(La_2S_3)_{0.35}(Er_2S_3)_{0.05}$, $(Ga_2S_3)_{0.60}(La_2S_3)_{0.30}(Er_2S_3)_{0.10}$, $(Ga_2S_3)_{0.60}(La_2S_3)_{0.27}(Er_2S_3)_{0.13}$, $(Ga_2S_3)_{0.60}(La_2S_3)_{0.25}(Er_2S_3)_{0.15}$ composite glasses respectively 4.0678; 4.1597; 4.1806; 4.1946 gr/cm^3, which obtained in a $(Ga_2S_3)_{0.60}(La_2S_3)_{0.40}$ glass by replacing the amount of La_2S_3 with Er_2S_3.

Boundaries of glass formation area in La_2S_3-Ga_2S_3-Er_2S_3 quasi-ternary system (fig. 1 (c)) determined by physical-chemical analysis methods – XRD, XRM, EDX, DTA, TGA. Diffractograms of primary components and alloys in a La_2S_3-Ga_2S_3-Er_2S_3 quasi-ternary system given in figure 10. X-Ray Diffractions confirms that both components $(Ga_2S_3)_{0.60}(La_2S_3)_{0.35}(Er_2S_3)_{0.05}$ containing transparent and $(Ga_2S_3)_{0.60}(La_2S_3)_{0.27}(Er_2S_3)_{0.13}$ containing non-transparent glasses are amorphous (fig.10).

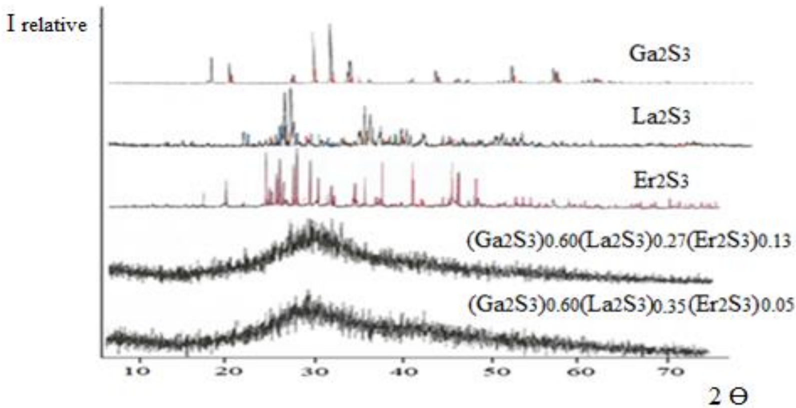


Figure 10. Diffractograms of primary components and alloys in a La_2S_3-Ga_2S_3-Er_2S_3 quasi-ternary system

However, comparing the diffraction patterns of these samples, it is clear that the degree of crystallization in the diffraction pattern of opaque glass is relatively high (41.7% per device). This confirms that the opacity is related to the crystal centers in the composition.

Scanning Electronic images in powder form of primary components and $(Ga_2S_3)_{0.60}(La_2S_3)_{0.35}(Er_2S_3)_{0.05}$ containing transparent glass from the La_2S_3-Ga_2S_3-Er_2S_3 quasi-ternary system are provided (fig.11).

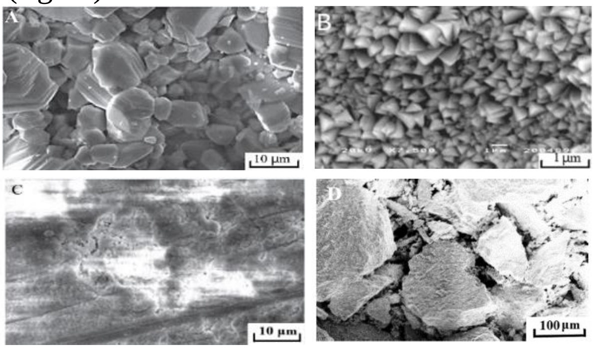


Figure 11. Scanning Electronic images of primary components and $(Ga_2S_3)_{0.60}(La_2S_3)_{0.35}(Er_2S_3)_{0.05}$ glass. A-Ga_2S_3, B-La_2S_3, C-Er_2S_3, D-$(Ga_2S_3)_{0.60}(La_2S_3)_{0.35}(Er_2S_3)_{0.05}$ glass

The figure shows that the microrelief of $(Ga_2S_3)_{0.60}(La_2S_3)_{0.35}(Er_2S_3)_{0.05}$ glass is different from the original components.

Figure 12 shows the results of quantitative element analysis of $(Ga_2S_3)_{0.60}(La_2S_3)_{0.35}(Er_2S_3)_{0.05}$ transparent glass by EDX method.

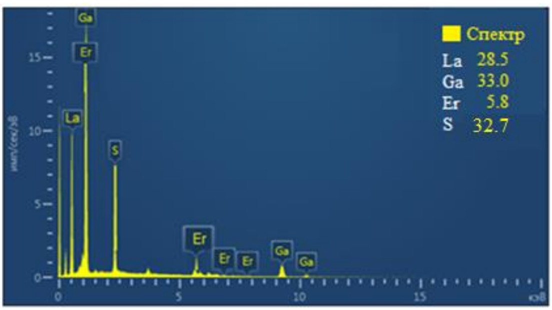


Figure 12. Quantitative element analysis of $(Ga_2S_3)_{0.60}(La_2S_3)_{0.35}(Er_2S_3)_{0.05}$ transparent glass by EDX method

The results of the analysis correspond to the stoichiometric composition of the glass.

To study the thermal resistance of $(Ga_2S_3)_{0.60}(La_2S_3)_{0.35}(Er_2S_3)_{0.05}$ composite glass are drawn the dynamic air derivatogram and the differential calorimetric (DSC) thermogram in inert medium (He) of the 400 mg sample (figures 13 and 14).

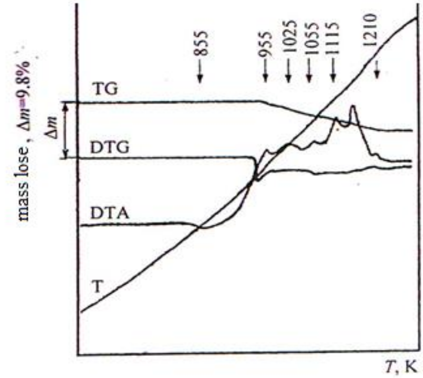


Figure 13. Air derivatogram of $(Ga_2S_3)_{0.60}(La_2S_3)_{0.35}(Er_2S_3)_{0.05}$ glass

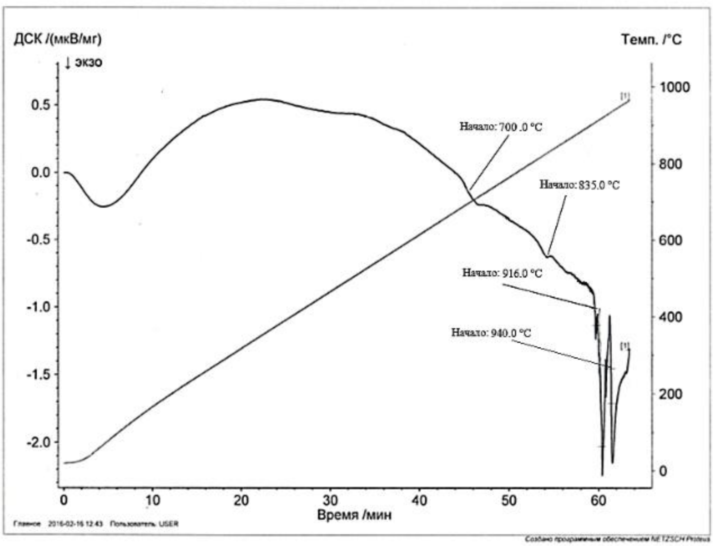


Figure 14. Differential Scanning Calorimetric (DSC) Thermogram of $(Ga_2S_3)_{0.60}(La_2S_3)_{0.35}(Er_2S_3)_{0.05}$ glass in inert (He) medium

As can be seen from the derivatogram in figure 13, softening process of $(Ga_2S_3)_{0.60}(La_2S_3)_{0.35}(Er_2S_3)_{0.05}$ glass occurs at 855 K. Exoeffects and mass loss in the temperature range 955÷1250 K indicate that the stepwise mechanism decomposition of glass.

Mass lose is: $\Delta m = \frac{m_1 - m_2}{m_1} \cdot 100\% = \frac{400-356}{400} \cdot 100\% = 11\%$.

Crystallization temperature of glass was not observed during derivatographic analysis. In contrast to the derivatogram in the DSK thermogram, the crystallization of the glass occurs at T_k = 1110 K (835°C).

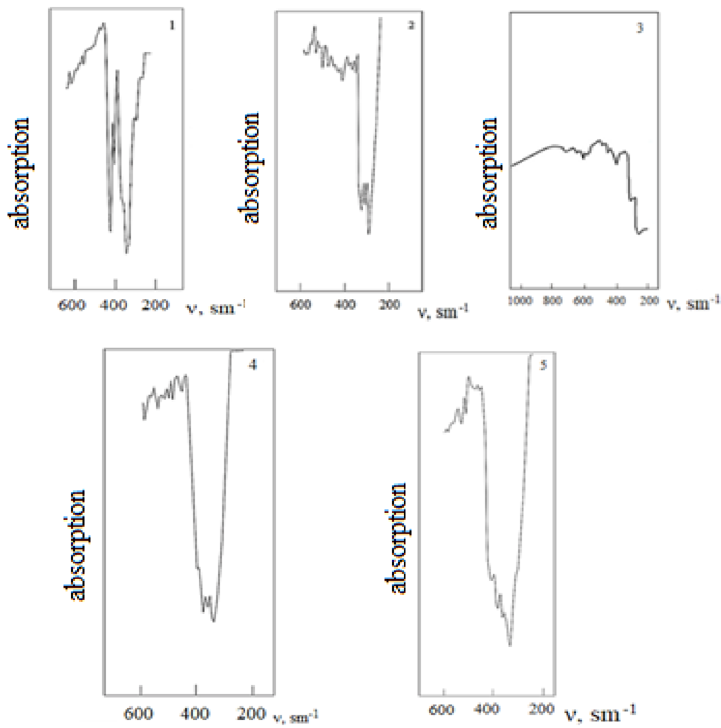


Figure 15. IR spectrum of primary components and glasses in La_2S_3- Ga_2S_3-Er_2S_3 quasi-ternery system: β-Ga_2S_3 (1), δ-Er_2S_3 (2),

α-La_2S_3(3), $(Ga_2S_3)_{0.60}(La_2S_3)_{0.35}(Er_2S_3)_{0.05}$ (4),
$(Ga_2S_3)_{0.60}(La_2S_3)_{0.27}(Er_2S_3)_{0.13}$ (5)

The softening temperature is in the range of T_g = 975K (700 °C) and the decomposition temperature is in the range of 1191÷1215 K (916÷940 °C) (fig. 14). Therefore, $(Ga_2S_3)_{0.60}(La_2S_3)_{0.35}(Er_2S_3)_{0.05}$ glass is thermally resistant in inert (He) mediun at 975 K (700 °C) and in air at 855 K (580 °C).

Figure 15 shows the IR spectra of the primary components (β-Ga_2S_3, α-La_2S_3, δ-Er_2S_3) and $(Ga_2S_3)_{0.60}(La_2S_3)_{0.35}(Er_2S_3)_{0.05}$, $(Ga_2S_3)_{0.60}(La_2S_3)_{0.27}(Er_2S_3)_{0.13}$.

At the characteristic IR frequencies of the primary components of Ga_2S_3 and La_2S_3, the frequencies corresponding to the glass are practically undetectable. It can be assumed that the Ga atoms in the glass have the same tetrahedral local range and are coordinated with the sulfur atoms as in the crystal analogue, and that this bond is more covalent than the original components. The transition of the bands in the glass to a higher frequency range than in the case of individual compounds is most likely due to the strengthening of the Ga − S bond, as shown above. Due to the local coverage of La^{3+} ions in the glass, we note the following points. A comparison of the IR frequencies of the La − S bond in the glass and the primary component, La_2S_3, allows us to state that in both cases, Lanthan has a similar symmetry of the local environment and the same coordination numbers. It should be noted that in this case, the resulting glass Er^{3+} (Er_2S_3) ions replace some of the La^{3+} ions (La^{3+} and Er^{3+} ion radii are 1.04 and 0.85 Å, respectively).

Note that glass containing $(Ga_2S_3)_{0.60}(La_2S_3)_{0.40}$ is a good enough matrix to obtain triple glass by activating it with Ln^{3+} ions. Thus, effective luminescence samples can be obtained by incorporating Ln^{3+} ions into a binary glass $(Ga_2S_3)_{0.60}(La_2S_3)_{0.40}$.

In the **Nd_2S_3-Ga_2S_3-EuS** quasi-ternary system [3, 5, 6, 13, 14], the boundaries of the glass formation area were determined by studying 35 samples synthesized from primary components under sulfur vapour pressure by XRD, XRM, EDX, DTA, STA methods (Fig. 1. (e)).

Figure 1 (e) shows that in the Nd_2S_3-Ga_2S_3-EuS quasi-ternary system, the glass formation area starts at 24÷46 mol /% on the Ga_2S_3-Nd_2S_3 side and ends at 9÷26 mol /% on the Ga_2S_3−EuS side. Of the 35 samples from the glass formation area, 9 correspond to the hatched-opaque glass area, which borders the transparent glass formation area on both sides, and 26 to the dark-colored transparent glass area.

Nd_2S_3-Ga_2S_3-EuS quasi-ternary system the color of the glass change from light brown to dark brown starts from Ga_2S_3 −Nd_2S_3 side and depending on the amount of EuS (fig. 16).

Figure 16. Photo description of the $(Ga_2S_3)_{0.65}(Nd_2S_3)_{0.20}(EuS)_{0.15}$ glass in the Nd_2S_3-Ga_2S_3-EuS quasi-ternary system

Samples from the glass formation area are partially decomposed at room temperature under the influence of alkali and mineral acids. Resistant to water and organic solvents at room temperature.

In the Nd_2S_3-Ga_2S_3-EuS quasi-ternary system by keeping the amount of Ga_2S_3 constant starting from the $(Ga_2S_3)_{0.70}(Nd_2S_3)_{0.30}$ composition the density of the constituent glasses $(Ga_2S_3)_{0.70}(Nd_2S_3)_{0.25}(EuS)_{0.05}$, $(Ga_2S_3)_{0.70}(Nd_2S_3)_{0.20}(EuS)_{0.10}$, $(Ga_2S_3)_{0.70}(Nd_2S_3)_{0.15}(EuS)_{0.15}$, $(Ga_2S_3)_{0.70}(Nd_2S_3)_{0.10}(EuS)_{0.20}$, $(Ga_2S_3)_{0.70}(Nd_2S_3)_{0.07}(EuS)_{0.23}$ according to 4.0046; 4.0199; 4.0353; 4.0508; 4.0664 və 4.0758 g/cm^3.

The XRD reaffirms that the opacity of the glass in the area indicated by the hatched strip in the glass formation area ($m_1m_2m_1'm_2'$) in figure 1 (e) is due to the presence of crystal centers in the composition (fig.17).

Diffraction patterns were not observed in the diffractogram of transparent glass $(Ga_2S_3)_{0.70}(Nd_2S_3)_{0.25}(EuS)_{0.05}$ (fig.17). Observation of low-intensity diffraction lines in the diffractogram of opaque glass containing $(Ga_2S_3)_{0.65}(Nd_2S_3)_{0.15}(EuS)_{0.20}$ once again confirms the presence of crystal centers in the composition (in the example, the crystallization rate is 41.7% per device).

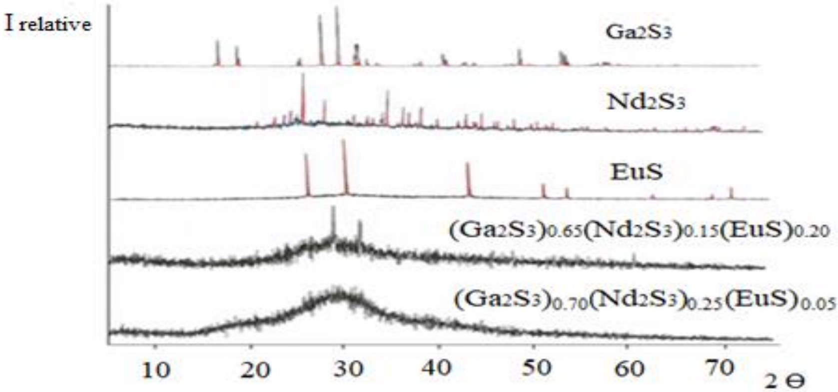


Figure 17. Diffractograms of primary components and alloys in the Nd_2S_3-Ga_2S_3-EuS quasi-ternary system

A comparative description of the Scanning Electron Microscope of $(Ga_2S_3)_{0.70}(Nd_2S_3)_{0.25}(EuS)_{0.05}$ transparent glass with the primary components is shown in figure 18.

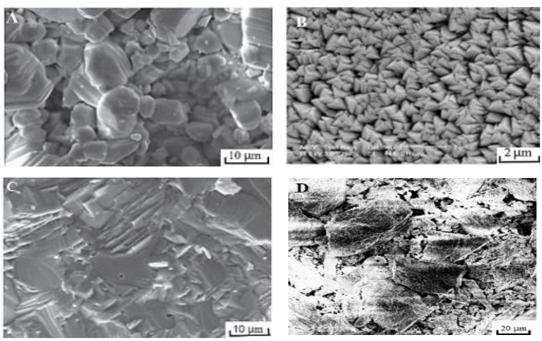


Figure 18. Description of primary components and $(Ga_2S_3)_{0.70}(Nd_2S_3)_{0.25}(EuS)_{0.05}$ glass on a scanning electron microscope: A-Ga_2S_3, B-Nd_2S_3, C-EuS, D-$(Ga_2S_3)_{0.70}(Nd_2S_3)_{0.25}(EuS)_{0.05}$ transparent glass

The figure shows that the microrelief of $(Ga_2S_3)_{0.70}(Nd_2S_3)_{0.25}(EuS)_{0.05}$ transparent glass on a Scanning Electron Microscope is completely different from the primary components.

The results of quantitative element analysis of $(Ga_2S_3)_{0.70}(Nd_2S_3)_{0.25}(EuS)_{0.05}$ transparent glass by EDX method of are given in figure 19.

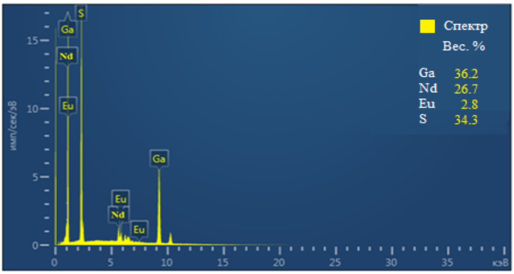


Figure 19. The quantitative element analysis of $(Ga_2S_3)_{0.70}(Nd_2S_3)_{0.25}(EuS)_{0.05}$ transparent glass by EDX method

The results of the analysis correspond to the stoichiometric composition of the glass.

The DSC method was used to determine the thermal stability of the obtained transparent glass. Figure 20 shows a thermogram of an inert medium (He) of $(Ga_2S_3)_{0.70}(Nd_2S_3)_{0.25}(EuS)_{0.05}$ transparent glass.

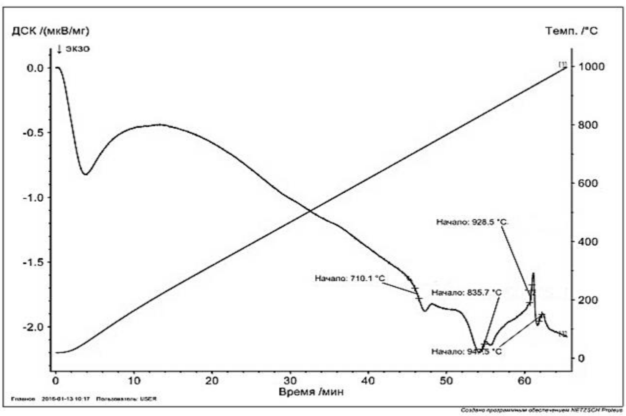


Figure 20. Differential Scanner Calorimetric (DSC) thermogram of $(Ga_2S_3)_{0.70}(Nd_2S_3)_{0.25}(EuS)_{0.05}$ glass in an inert (He) medium

It is clear from the thermogram that the glass under study begins to soften at Tg = 1010 K (735 °C) and crystallizes at T_k = 1110 K (835 °C). Exoeffets occurring at 1145÷1225K (870 ÷ 950 °C) characterize the gradual fragmentation of glass.

Figure 21 shows the IR absorption spectra of glass samples and primary components. It can be seen from the spectrum that the intense bands characterizing the valence oscillations of the Me − S bond in the 200÷360 cm^{-1} region of the Ga_2S_3, Nd_2S_3, EuS IR spectrum are almost identical.

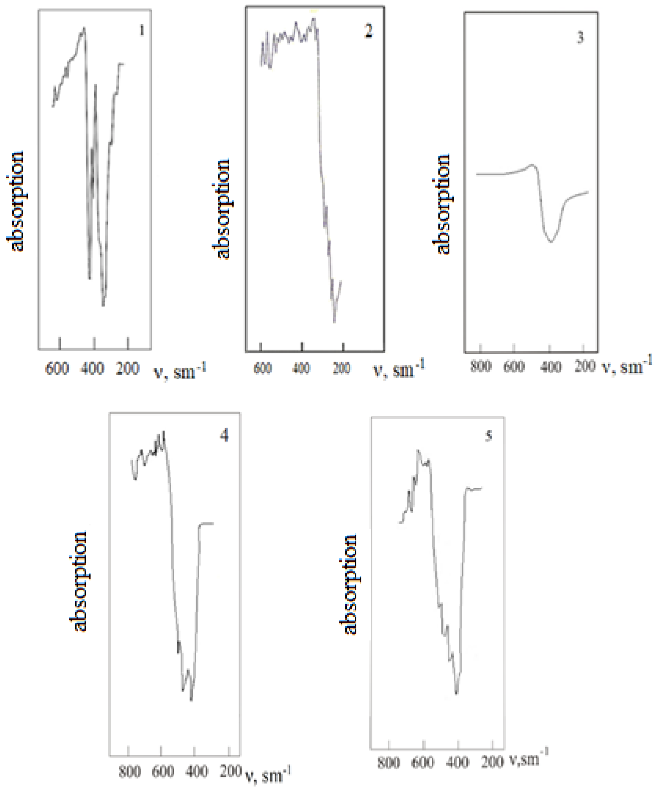


Figure 22. IR spectrum of primary components and glass in the Ga_2S_3-Nd_2S_3-EuS quasi-ternary system: β-Ga_2S_3 (1), Nd_2S_3 (2), EuS (3), $(Ga_2S_3)_{0.70}(Nd_2S_3)_{0.25}(EuS)_{0.05}$ (4), $(Ga_2S_3)_{0.65}(Nd_2S_3)_{0.15}(EuS)_{0.20}$ (5)

However, in the Ga_2S_3 and EuS spectra, these bands are in the higher frequency range - 260 ÷ 480 cm^{-1}. observed, EuS dances 178 and 266 cm^{-1}. As can be seen from figure 21, the strips are the same at 400 cm^{-1} for Ga_2S_3 and glass.

In addition, the spectra of these sulfides show low-intensity bands in the range 540÷750 cm^{-1}, which are probably related to the valence oscillations of the Me−S bond. It should be noted that compared to the spectra of sulfides of the primary components, an increase in the intensity of these ranges and a transition to a high-frequency field are observed in the spectrum of clear glass containing $(Ga_2S_3)_{0.70}(Nd_2S_3)_{0.25}(EuS)_{0.05}$. As can be seen, this is also due to the increase in covalence in the bonds and the formation of new Me−S bonds in the glass.

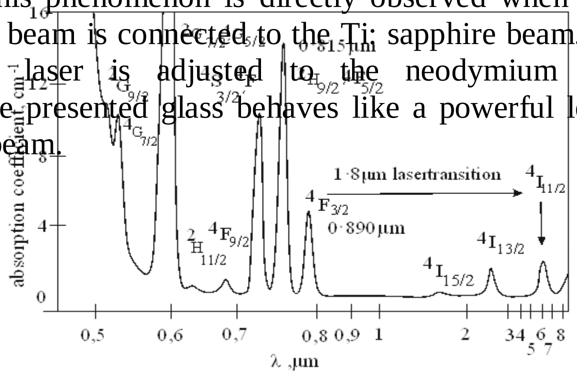
In the fourth chapter (7p.) are given the results of the study of photoluminescence and optical properties of lanthanides with gallium-mixed cationic sulfide glass $(Ga_2S_3)_{0.70}(Nd_2S_3)_{0.25}(EuS)_{0.05}$ and $(Ga_2S_3)_{0.80}(Er_2S_3)_{0.05}(EuS)_{0.15}$.

1.40 mm thick polished sample made of $(Ga_2S_3)_{0.70}(Nd_2S_3)_{0.25}(EuS)_{0.05}$ transparent glass with a normal absorption spectrum up to the level of $^4I_{11/2}$ at a wavelength of 5.2 μm at 300 K (fig. 22).

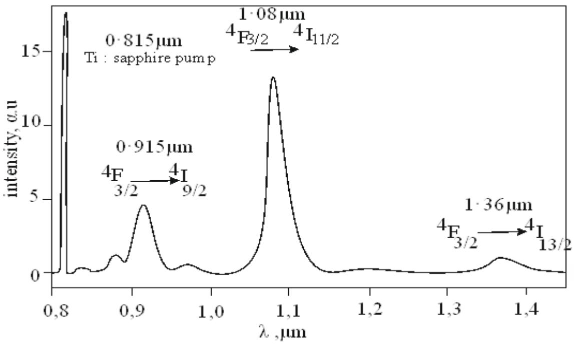
Ti:sapphire and He/Ne lasers were used to excite the sample. Various input devices with a radius of 50 mm and a hemisphere reactor with a high reflectivity of 1.08 μm were used for laser experiments. The glass sample is placed tightly on the surface of the mirror.

The spectrum covers a wide area from the UV absorption area - from 0.5 microns to 8 microns. There are 0.815 and 0.890 μm absorption bands corresponding to the $^4H_{9/2}$, $^4F_{5/2}$, upper $^4F_{3/2}$ laser levels and the $^4F_{3/2}\rightarrow{}^4I_{11/2}$ transitions. A small absorption coefficient at 0.890 μm reduces the thermal loading of the glass and further increases the homogeneous vibration in the sample.

Depending on the wavelength, it is absorbed by 88% at 0.815 μm and 50% at 0.890 μm. In sulfide glass, changes in the dn/dT temperature index and high thermal expansion increase the optical properties. This phenomenon is directly observed when the He/Ne infrared laser beam is connected to the Ti; sapphire beam. When the Ti: sapphire laser is adjusted to the neodymium absorption frequency, the presented glass behaves like a powerful lens for the He/Ne laser beam.



a)



b)

Figure 22. Normal absorption (a) and photoluminescence (b) spectra of the $(Ga_2S_3)_{0.70}(Nd_2S_3)_{0.25}(EuS)_{0.05}$ glass at 300 K

The absorption coefficient of the $^4F_{3/2}$ level (2.0 mm) is three times greater than the absorption coefficients of the $^2H_{9/2}$ and $^4F_{5/2}$ levels (0.7 mm). The photoluminescence property of Nd^{3+} ion was measured at 0.815 μm by excitation of $^2H_{9/2}$, $^4F_{5/2}$ using a Ti:sapphire laser. In this case, multifonon radiation is associated with the transition from $^2H_{9/2}$, $^4F_{5/2}$ to $^4F_{3/2}$ within 70 μs. The laser spectrum is shown separately in figure 22 b. It is clear from the figure that the maximum of the laser radiation corresponds to a wavelength of 1.08 μm and is associated with the transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$.

Thus, for the first time we studied the laser properties of a glass $(Ga_2S_3)_{0.70}(Nd_2S_3)_{0.25}(EuS)_{0.05}$. It was found that the studied sample showed laser properties at a wavelength of 1.08 μm at room temperature. It can be used as a laser element in the manufacture of 1.3 μm wavelength amplifiers for telecommunications in fiberglass communication systems. However, the laser properties of Nd^{3+} ions in glass are weak compared to corresponding crystalline matrices. This is due to the relatively high beam loss in glass. It may be possible to improve the quality of the laser due to the optimal activator density and the length of the sample. In addition, the photoluminescence spectrum of transparent glass excited at room temperature
(λ=331.1nm) $(Ga_2S_3)_{0.80}(Er_2S_3)_{0.05}(EuS)_{0.15}$ is shown in figure 23.

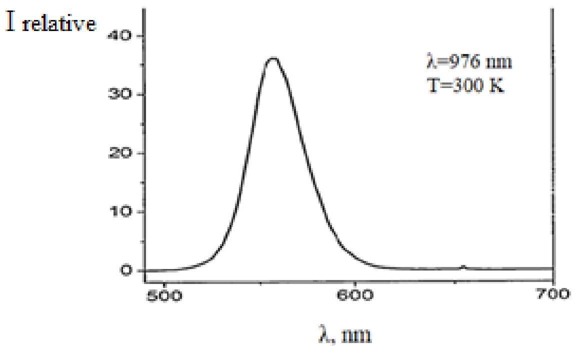


Figure 23. In the visible and IR field of the spectrum
($\lambda_{excit.}$ = 337.1 nm, T = 300K) $(Ga_2S_3)_{0.80}(Er_2S_3)_{0.05}(EuS)_{0.15}$

radiation spectrum of composite glass

The wide band with a maximum of 550 nm shown in the figure corresponds to the 4f →5d transition occurring in the Eu^{2+} ion. Strips with maximums of 650÷700, 800÷850, 850÷950 and 950÷1000 nm occur in the Er^{3+} ion $^4F_{9/2} \rightarrow {}^4I_{15/2}$, $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$, $^4I_{11/2} \rightarrow {}^4I_{15/2}$ characterizes the transitions.

Figure 24 shows the FL spectrum observed when a sample of $(Ga_2S_3)_{0.80}(EuS)_{0.15}(Er_2S_3)_{0.05}$is excited by a beam of λ = 976 nm.

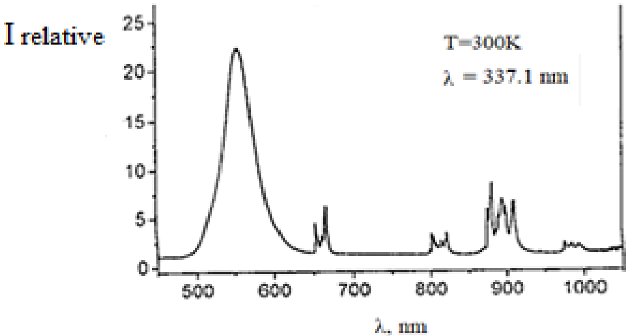


Figure 24. Antistox luminescence spectrum in $(Ga_2S_3)_{0.80}(EuS)_{0.15}(Er_2S_3)_{0.05}$glass

As can be seen from the spectrum, the sample here emits a broadband radiation covering an area of 500 ÷ 600 nm. In other words, antistox luminescence is observed in this sample. That is, radiation is transformed from the IR field into the visible field.

Thus, antistox radiation was observed during excitation (λ=976 nm) in a glass containing $(Ga_2S_3)_{0.80}(Er_2S_3)_{0.05}(EuS)_{0.15}$. That is, radiation has been transformed from an IR field into a visible field. This allows the composition to be used as an antistox phosphor in fiber-optic communication lines and night vision devices.

MAIN RESULTS

1. Differential Thermal (DTA), Thermal Gravimetric (TGA), Simultaneous Thermal (STA), X-Ray Diffraction (XRD), Scanning Electron Microscopic - SEM (X-Ray Microanalysis (XRM), Energy-Dispersion X-ray (EDX)) analysis methods and density measurement in the quasi-ternary systems $La_2S_3 - Ga_2S_3 - Ln^1_2S_3$ (Ln=Nd,Sm,Er) and $Ln_2S_3 - Ga_2S_3 - EuS$ (Ln=La,Nd,Sm,Er) the boundaries of the glass formation area are defined.
2. The color of the obtained glasses varies depending on the amount of Ln^{3+} ion and the thickness of the sample. Thus, in $La_2S_3 - Ga_2S_3 - Ln^1_2S_3$ quasi-ternary systems, the color of the glass on the $Ga_2S_3 - La_2S_3$ concentration plane depends on the amount of $Ln^1_2S_3$ and the thickness of the sample.
3. A comparative analysis of the differential thermal gravimetric (in air), synchronous thermal (in He environment) thermolysis of the obtained glass shows that softening temperature of glass in derivatographic analysis (Tg) (in He environment) is lower than the softening temperature determined in synchronous thermal analysis (for example, for the system $La_2S_3 - Ga_2S_3 - Nd_2S_3$ it is 880 K in the derivatogram, 1003 K in the STA). Tk cannot be determined in the derivatogram, it is determined in STA, which is due to the fact that the crystallization temperature of the glass in the derivatograph is close to the oxidation temperature in air.

4. The studied transparent glass formation areas are bounded on both sides by opaque glass areas. The visibility of the glass is opaque due to the formation of crystalline centers in the composition. Indeed, the high degree of crystallization of these glasses compared to clear glass has been confirmed once again by XRD.
5. The shift of the corresponding IR absorption spectrum bands of sulfide glasses to the high frequency region, compared to the primary components, is probably due to the increase of covalency in the Me–S bond in the glasses.
6. The absorption spectrum of $(Ga_2S_3)_{0.70}(La_2S_3)_{0.25}(Nd_2S_3)_{0.05}$ glass, visible at 300 K and in the near IR field, covers a wavelength of 0.5÷8 μm. The corresponding radiation bands of the $^2H_{9/2}$, $^4F_{5/2}$ levels of this field fall on the wavelengths of 0.815 and 0.890 μm. The laser radiation corresponding to a maximum wavelength of 1.08 μm is caused by the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition of the Nd^{3+} ion. The weakness of the laser property of the alloy Nd^{3+} ion in comparison with the corresponding crystalline matrices $(Ga_2S_3)_{0.70}(La_2S_3)_{0.25}(Nd_2S_3)_{0.05}$ is due to the relatively high beam loss in glass. It is possible to improve the quality of the laser by changing the optimal density of the activator.
7. Antistox radiation was observed when the $(Ga_2S_3)_{0.80}(Er_2S_3)_{0.05}(EuS)_{0.15}$ glass was excited (λ = 976 nm). That is, radiation has been transformed from an IR field into a visible field. This allows the composition to be used as an antistox phosphor in fiber-optic communication lines and night vision devices.

The main content of the dissertation is published in the following scientific works:

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The defense will be held on “**11**” “**January**” “**2024**” at “10^{00}” at the meeting of the Dissertation council ED 1.15 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at Institute of Catalysis and Inorganic Chemistry named after academician M. Nagiyev ry of Science and Education Republic of Azerbaijan.

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Dissertation is accessible at the Library of Institute of Catalysis and Inorganic Chemistry named after academician M.Nagiyev of Ministry of Science and Education Republic of Azerbaijan.

Electronic versions of dissertation and its abstract are available on the official website of the Institute of Catalysis and Inorganic Chemistry named after academician M. Nagiyev of Ministry of Science and Education Republic of Azerbaijan.

Abstract was sent to the required addresses on “**08**” “**December**” “**2023**”

Signed for print: 16.11.2023
Paper format: A5
Volume: 36161 signs
Number of hard copies: 20 copies
Published in the printing house of MSERA