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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

LUMINESCENCE PROPERTIES OF $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ SOLID SOLUTIONS

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GENERAL DESCRIPTION OF THE WORK

Relevance of the research topic. Recently the transition from binary compounds to multicomponent complex compounds are continues rapidly in semiconductor material science. These compounds allows to obtain high effective materials for use in various fields of science and technology. Such materials are capable to be widely used in optoelectronics, quantum electronics and laser techniques. Moreover, these type of materials also provides great opportunities for the description of information, energy-saving light sources, the development of high efficiency multi-purpose semiconductor lasers.

Modern lighting systems requires high-brightness white light sources to conserve electricity. High-efficiency luminescent materials that convert the blue light into white light are required to obtain white light sources created basis of blue light emitting diodes. Alkaline earth chalkogenides with complex structure are very promising as the basis of such type of luminescent materials. Unlike the traditional methods used so far, there is a strong interest in the creation and improvement of white light sources.The light sources made on the basis of the investigated materials are very different from previous lighting technologies, in terms of energy efficiency, durability and environmental purity.

Rare-earth doped semiconductor materials are widely used as phosphors and are very promising to obtaining non-coherent light sources. REE are create deep local levels and radiation centers at the bandgap of the semiconductors and this cause to high photosensitivity and efficiency luminescence at visible and infrared range of the light. The development of new phosphors based on the REE doped broadband semiconductors and determination of the effect of laser excitation on the FL spectrum, decay kinetics and efficiency is very important in both scientific and practical point of view.The solution of this problem will provide important information on the use of these substances in new light sources as phosphors.

Rare-earth activated MGa_2S_4 (M = Ca, Ba, Sr) type semiconductor compounds are widely used as phosphors and very promising to formation strong non-coherent radiation sources. REE are creates deep local levels and emission centers in the bandgap of the semiconductors and this cause to high photoconductivity and high efficiency photoluminescence in visible and infrared range of light. In this regard, the development of new phosphors based on NTE-activated MGa_2S_4 (M = Ca, Ba, Sr) semiconductors and the determination of the effect of laser excitation on the photoluminescence (FL) spectrum, decay kinetics and efficiency are both scientifically and practically relevant. The solution of this problem will provide important information on the use of these compounds as phosphors in the new radiation sources.

It is known that along optical and radiospectroscopy methods the important information about the defects in crystals also can be obtained by thermoactivation spectrocopy method. One of the thermoactivation spectroscopy method is thermoluminescence (TL). The TL is one of the most effective method to investigate trap levels in bandgap of materials.Thermoluminescence phenomenon is widely used in radiation dosimeters, age determination of archeological excavations in geology and in many other areas.

The PL and TL properties of MGa_2S_4 (M = Ca, Ba, Sr) typeternary compounds have been studied extensively by world scientists.Recently, numerous experiments were carried out to control light wavelength in wide range using MGa_2S_4-$M'Ga_2S_4$ (M, M' - Ba, Sr, Ca) type complex materials created by partial substitutions of alkaline-earth metals of close ionic radii. However, the investigations on the study of the PL and TL properties of such types of complex compounds is insufficient and more extensive research is needed in this direction.

The dissertation work was performed according to the scientific research plan of the Institute of Physics named after Abdullayev of Azerbaijan National Academy of Sciences.

Purpose and objectives of the study.

The purpose of the study is to study the effect of extarnal sources having different wavelengths on the photoluminescence spectra of Ca $(Al_xGa_{1-x})_2S_4:Eu^{2+}$ (x = 0; 0.1 ... 1) solid solutions, the determination of the effect of $Eu2^+$ ion on the photoluminescence of solid solutions in the range of wide temperature (10 ÷ 300 K) and power density ($3.5 \cdot 10^2 \div 1.4 \cdot 10^6$ W/cm^2), as well as the determination of the photo-thermoluminescence mechanisms and electronic transitions.

The following tasks were set to achieve this goal:

- ✓ Synthesis of $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions at x = 0, 0.1, 0.2, ... ,0.9, 1;
- ✓ Investigationinfluence of differentconcentration of Eu^{2+} ion to photoluminescence of $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions;
- ✓ Study of PL and PL excitation spectra of $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions at room temperature;
- ✓ Study of photoluminescence spectra of $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions in the wide range (10÷300K) of temperature;
- ✓ Investigation of TL spectra of $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions;
- ✓ Study of PL spectra of $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions in the wide range ($3{,}5\cdot10^2 \div 1{,}4\cdot10^6$W/cm^2) of power density;
- ✓ Investigation of PL kinetics depending on power density of external source;
- ✓ Determination of PL decay and influence of the temperature to lifetime;
- ✓ Determinationan efficiency of $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions at 20K and 300K temperatures.

Research objects and methods:

$Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ ($0\leq x\leq 1$; Eu^{2+} − 3;5;7 at%) solid solutions were selected as a research objects for performing of dissertation. The materials were synthesized by solid state reaction and x-ray diffraction and differential thermal analysis methods were

used to investigate structural properties. The xenon lamp with continuous radiation (230 – 550 nm), 3rd harmonic Nd:YAG laser (355 nm) and N_2 laser (337.1 nm) were used as excitation source to investigate PL properties of the samples. Analysis of the TL properties were performed on the ТЛГ-69М device using ПРК-4 mercury lamp as an excitation source. The Lushik method, Urbach method, Randal method and Garlick-Gibson method were used for the study of TL spectra.

Main provisions for the defense

1. PL spectra are shifted to the short wavelengths due to shifting 5d gravity center of the Eu^{2+}under the influence of the crystal field when the amount of the Al cation increase in the $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions.
2. The PL peaks of $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions are formed due to the electronic transitions from $4f^65d$ excited state to $^8S_{7/2}$ initial state of Eu^{2+} ions and PL intensity increase up to 3 times with increasing the amount (from 3% to 7%) of the Eu^{2+} ions in $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions. The position and shape of the PL spectra does not change due to the stable crystal environment around the Eu^{2+} ion in crystals.
3. The reason for decreasing of PL intensity and the expansion of the full width at half maximum of PL spectra (FWHM) is due to the increase of $n \rightarrow m$ energy transitions by increasing of vibrational energies of the initial (m) and excited (n) states when increasing the temperature.
4. The position and the shape of the PL spectra of $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions are not change by increasing in the range of $3{,}5\cdot10^2 \div 1{,}4\cdot10^6$ W/cm^2 power densitiy. PL efficiency remains stable in the range of $3\cdot10^2 \div 2\cdot10^4$ Vt/sm^2 power density and begins to decrease after $2\cdot10^4$ Vt/sm^2.
5. Although, the PL decay kinetics in $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions obey exponentional law below $2\cdot10^4$ W/cm^2 power densities, the fast components appears together with slow

components in PL decay kinetics due to absorbtion from excited levelwhen the excitation levels higher than $2 \cdot 10^4$ W/cm^2.

6. TL spectra are changes and additional TL peaks are observed when partial substitutions of Al ions with Ga ions in the $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions.

The scientific novelty of the research:

- ✓ It has been shown that observed blueshift (44 nm) withchanging the value of the x in $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions is due to the change in the crystal field with varying cation concentration.
- ✓ It was determined that the positions of the PL maxima are not change depending on the temperature (10 ÷300 K) and power density ($3.5 \cdot 10^2 \div 1{,}4 \cdot 10^6$ Vt/sm^2) of the external excitation source.
- ✓ The lifetime measurements at higher than $2 \cdot 10^4$ Vt/sm^2 power density showed that the fast components are formed in the background of the slow components at $4f^65d$ excited level in the $Ca(Al_xGa_{1-x})_2S_4$solid solutions.
- ✓ The stable and decreased ranges of PL efficiency depending on the power density were determined for $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions.
- ✓ The electron transitions of Eu^{2+} ions that cause emission in the studied $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions were determined and the diagram showing the energy state of Eu^{2+} ions in the crystal matrix has been constructed.
- ✓ The mechanisms of the persistent TL in the $Ca(Al_xGa_{1-x})_2S_4$ and $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions were investigated and the possibility of the increasing in the duration of persistent luminescence due to Eu^{2+} ion, as well as defects has been shown.

The theoretical and practical significance of the research:

The results obtained in the dissertation shown that the $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions can be used to create tunable lasers in the range of green to yellow part of light, in the solid state

electronics, lighting, catod-ray tubes, field emission displays, photodiodes (PD) and light emitting diodes (LEDs), as well as to create and development of new generation solid state lasers.

Some part of the experiments on the dissertation were carried out within the framework of the following grant projects.

1. EİF-BGM-2-BRFTF-1-2013. "Random lasers, wideband semiconductors and rare-earth activated chalkogenide crystals, luminescence and optical properties of nano- and micropowders at optical and electron excitation".

2. EİF-BGM-3-BRFTF-2+(2017)-393. "Coherent and non-coherent monochromatic and white light sources based on wideband chalcogenide and II-VI type semiconductors activated with rare earth elements"

Approbation and implementation:

The main results of dissertation work were discussed at the following national and international conferences and seminars:

- ✓ IX international conference "Amorphous and Microcrystalline Semiconductors",2014, St. Petersburg, Russia;
- ✓ X international conference "Amorphous and microcrystalline semiconductors", 2016, St. Petersburg, Russia;
- ✓ II international scientific conference of young researcher: dedicated to the 91rd anniversary of the national leader of Azerbaijan, Haydar Aliyev, april 18-19, 2014, Baku, Azerbaijan
- ✓ XXIII international conference of students, graduate students and young scientists, "Lomonosov-2016", Section "Physics", April 11–15, 2016, Moscow, Russia.
- ✓ IX international conference "Opto-, nanoelectronics, condensed environment and high energy physics",december 25-26, 2015, Baku, Azerbaijan.
- ✓ International conference on"Modern trends in physics", april 20–22, 2017, Baku, Azerbaijan.
- ✓ XXIII international conference of students, graduate students and young scientists, "Lomonosov-2018", Section "Physics", april 9–13, 2018, Moscow, Russia.

- ✓ Academician G.B. Abdullayev centenary international conference and school “Modern Trends in Condensed Matter Physics”, september 24-26, 2018, Baku, Azerbaijan.

Publications: The main results obtained in the dissertation were published in 10 articles (5 of them are inlcuded SCI list with impact factor) and in 7 conference materials

Volume, structure and the main content of the dissertation:

The dissertation consist of the introduction, four chapters, results and the list of 158 used references.The scope of the work consists of 201139 characters, excluding figures, tables, graphs, appendices and references.

CONTENT OF WORK

In the introduction has been justified the relevance of the topic, the purpose of the work, scientific novelty, the main provisions for the defence are presented as well as the information about the international and national conferences are shown where the results of the work were discussed. Scientific and practical significance of dissertation and the short description of the chapters also presented in this section.

Chapter I is summary and dedicated to literature review of the synthesis, structure and luminescence properties of $A^{II}B_2^{III}C_4^{VI}$ type alkaline earth elements as well as the investigation of the luminescence properties of MGa_2S_4-$M'Ga_2S_4$ type solid solutions activated with REEs.

Chapter II is devoted to the synthesis method of the CaS, Ga_2S_3 və Al_2S_3 binary compounds and $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions. Binary compounds which used for the synthesis of $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions were synthesized in first step. There were some chemical processes to obtain CaS, Ga_2S_3 və Al_2S_3 compounds. The synthesis of CaS binary compound was carried out in the quartz reactor by the interaction of the finely dispersed powder of calcium carbonates ($CaCO_3$) under the influence of the hydrogen

sulfide (H_2S) and carbon sulfide (CS_2) steam. The process was carried out in the atmosphere of inert gas Ar during the 24 hours. The steam of the H_2S and CS_2 are derived from the decomposition of NH_4SCN (ammonium thiocyanate) at 250 ^{0}C temperature. The Ga_2S_3 and Al_2S_3 compounds were sythesized during the 2 hours by solid state reaction at high temperature and high vacuum in the quartz ampoule. The initial reagents for synthesis were chosen high purity Ga-99,999%, Al- 99,999 and S-99,999% .

The main components CaS, Al_2S_3 and Ga_2S_3 binary compounds of the phosphor materials were powdered and sieved from 25x25μm size, then carefully mixed in stoichiometric ratios and made into homogeneous. Obtained mixed compounds were filled in quartz ampoule, obtained high vacuum in the ampoule and synthesized at 1100 ± 10˚C temperature. The temperature of the furnace was regulated by the high-precision(Δt±0,5°C) BRT-2 temperature regulator.The synthesis was performed for 1 h, then the temperature of the furnace gradually cooling down 650 ± 5^{0}C and kept at this temperature for annealing during the 24 h. Annealing process lead to further improvement of the crystalline properties of the obtained polycrystals. Note that the Eu rare-earth element are included this matrixes as EuF_3.

The information about the diffractometer used for investigating crystal structure, as well as the devices for studying PL, PL excitation, PL kinetics and TL spectra also presented in this chapter.

The results of the x-ray analyzes of CaS, $Ga_2S_3$and Al_2S_3 compounds as well as $Ca(Al_xGa_{1-x})_2S_4$(x = 0.1 – 0.9) solid solutions and photoluminescence properties at 10 ÷ 300K temperature range under the 337,1 nm and 355 nm excitation wavelengths are presented in **chapter III.** X-ray analyzes of powder samples were performed at "XRD-D8 ADVANCE" diffractometer under the normal condition. The results of structural analyzes shown that the x-ray spectra of synthesized CaS, Ga_2S_3 and Al_2S_3 compounds are characteristic for these samples. The crystal parameters for each samplewere calculated and are given in the chapter.

Structural properties of $Ca(Al_xGa_{1-x})_2S_4$ semiconductor solid solutions were studied at room temperature. It has shown that the crystal structures of the $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions don't change depending on the concentration of the Al^{3+}cation and the phase transition was not observed by the increase of the value of *x*, i.e. all samples depending on *x* have the single phases.

The PL excitation and PL emission properties of solid solutions and compounds were studied using xenon lamp with continuous radiation (230 – 550 nm), Nd:YAG laser (355 nm) and N_2 laser (337.1 nm) as external excitation sources. It was shown that, the shape and the position of the maximum on the PL spectra of $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions do not depend on the wavelength of the excitation light. This means that photoluminescence is not depended on the source which is one of the indicates of stability of the sample as a phosphor.

The photoluminescence spectra of lanthanoid ions introduced into the crystal as activators are mainly associated with 4f → 4f and 4f → 5d electron transitions.While the 4f → 4f transition generates a spectrum oflinear radiation, the 4f → 5d electron transitions create a broadband of radiation. Note that Eu^{2+} is widely used rare earth elements and creates intense and broad spectrum in the range ultraviolet, visible and infrared wavelengths within various compounds.The energy of the $4f^65d^1$ excitation level depends on the crystal field, because the 5d electrons are not wellshielded with outer layer the lattice, therefore strongly influenced with lattice. Nevertheless, 4f electrons are well-shielded and not exposed to electron-phonon interactions within the lattice, so it is insignificant to forming the maxima corresponding to the 4f – 4f transitions.$4f \rightarrow 5d$transition cause forming broad bands. Because $4f^65d^1$ levels are decomposed by the crystal field and are strong interaction with lattice phonons, and it's lead to forming broad absorption and emission bands.

PL excitation and emission spectra were measured for $Ca(Al_{0,1}Ga_{0,9})_2S_4:Eu^{2+}$ solid solutions at room temperature using xenon lamp. PL excitation spectra is due to the $4f^7 \rightarrow 4f^6 5d$

electronictransitions of Eu^{2+}ions and covered in the wide range from 310 nm to 520 nm of the wavelength. The broadband PL emission spectra associated with the $5d \rightarrow 4f$ electronic transition of Eu^{2+} ions is covered in the range of 480 – 650 nm of the wavelength. Absorption spectra was established to determine Redshift (D) and stokes shift (ΔS) using mirror image rule which applied to the intersection point of the long wavelength part of excitation spectrum and short wavelength part of the emission spectrum. The values of the stokes shift were calculated based on the energies corresponded to the maximums of the absorption and PL emission spectra. The values of the redshift were calculated using energies corresponds to the maximums of the absorption and emission spectra and stokes shift.

PL intensity was increased up to 3 times in the range of 500 – 630 nm wavelength by increasing the amount of the Eu^{2+} from 3% to 7% in $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions (Fig. 1). It is clear from the figure that the positions of the maximums of PL spectra are not changed by increasing the amount of the Eu^{2+} ions in the $Ca(Al_xGa_{1-x})_2S_4$ matrix and the wavelength maximum of the PL spectra are situated on the ~558 nm. It means the shape of the PL spectra is not depend on the dopand concentration. However, the doping level is strongly influencedby PL intensity.

The reason for the absence of shifting at the maximums of the FL spectra is constant crystal environment around the Eu^{2+} ion, i.e., the host matrix does not change by changing amount of the Eu^{2+}. This proves again that, REE ions only influence on the luminescence properties of solid solutionsas an activator .

The PL maximums of the Eu^{2+} doped $Ca(Al_xGa_{1-x})_2S_4$ solid solutions has short-wavelength shift by 44 nm from 560nm for $x = 0$ to 516 nm for $x = 1$. The spectra are shifted by 44 nm and this indicate to the $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions have intense photoluminescence in the green-yellow spectral region.The short-wavelength shift of PL spectra formed by $4f^65d \rightarrow 4f^7$electron transitions of Eu^{2+} ions is due to the change of the energystate of Eu^{2+} ions as a result of the gradual substitutions of Ga atoms to Al

atoms. So that, the substitutions of Ga atoms to the same valency of Al atoms cause to increase of the electronegativity effect of kations and decrease of the polarization covalency between Eu^{2+} ions and anions. This cause to decrease in the centroid shift. The decreasing of the centroid shift is manifested by the blue shift in the emission peaks.

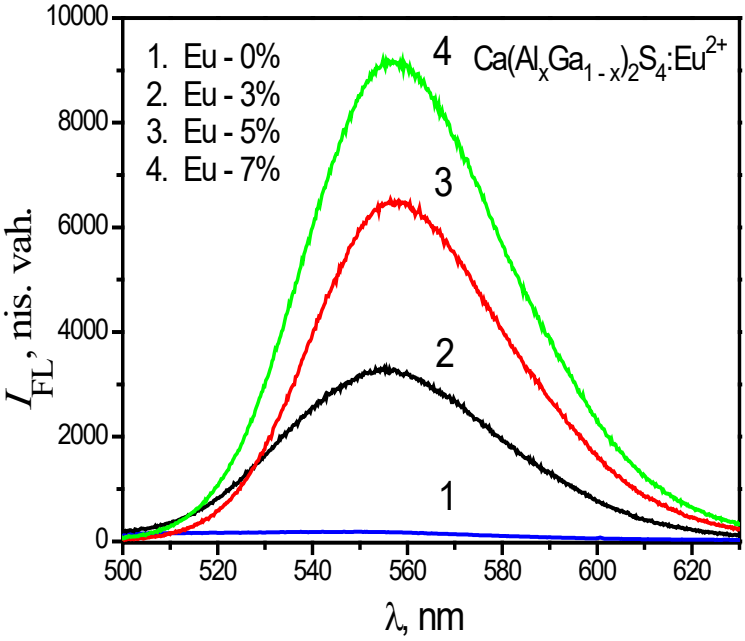

Figure. 1. Photoluminescence spectra of Eu^{2+} doped $Ca(Al_{0.1}Ga_{0.9})_2S_4$ solid solution at 300 K temperature.

It was determined that the PL spectra of the $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions are demonstrated high stability in the temperature range of 10 ÷ 300 K. The shape and the position of the maximum of spectra don't change. Also, the reduction of FL integrated intensities in this temperature range is below 35% for all *x*

values. The number of the transitions from an initial state to excited state is increased by increasing the temperature in the $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions and in the results, the PL spectra are expanded monotonously by 18 nm for all values of *x*.

Influence of γ-rays to PL properties of $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solution also studied in this chapter. The experiments have shown that both donor and acceptor centers are formed in different material by the effect of the ionizer beams. These, in turn, lead to the changes of many physical and chemical properties and ultimately allows to control the properties of the materials. Effect of the γ-rays on the PL properties of $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions have been investigated in the first time. $Ca(Al_{0,1}Ga_{0,9})_2S_4:Eu^{2+}$ solid solution was irradiated in the range of 250 – 1250 krad under the influence of the γ-rays with 1,33 MeV energy. Note that the FL spectra of the solid solution investigated in the range 250 to 1000 krad increase by ~ 2 times and the full width at half maximum (FWHM) of spectra are expanded. We have observed a decrease in PL intensity at the next dose. Radiation defects in $Ca(Al_{0,1}Ga_{0,9})_2S_4:Eu^{2+}$ crystals as a result of irradiation by γ - quantum create complexes with trace atoms in crystals which these complexes eliminate the capture centers for photoexcitedchargers. This causes the increase of the FL intensity in the crystalin the range of $D_\gamma = 250 – 1000$ krad. PL intensity of the crystal decreases due to increased defect concentration in subsequent values of irradiation doses.

The PL spectra of the $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions also were measured in a wide range ($3.5\cdot10^2 – 1{,}4\cdot10^6$ W/cm^2) of the power density of external exciting source (fig. 2). As seen from the figure, the shapes and maximum of the position of spectra don't change in the wide range of power density. The integral PL intensity and the full width at half maximums (FWHM) are increased by increasing the power density. We suppose that such an increase in intensity at a very high level of power is due to the better solubility of Eu^{2+} ions within the $Ca(Al_xGa_{1-x})_2S_4$ matrix and the formation of isolated radiation centers.

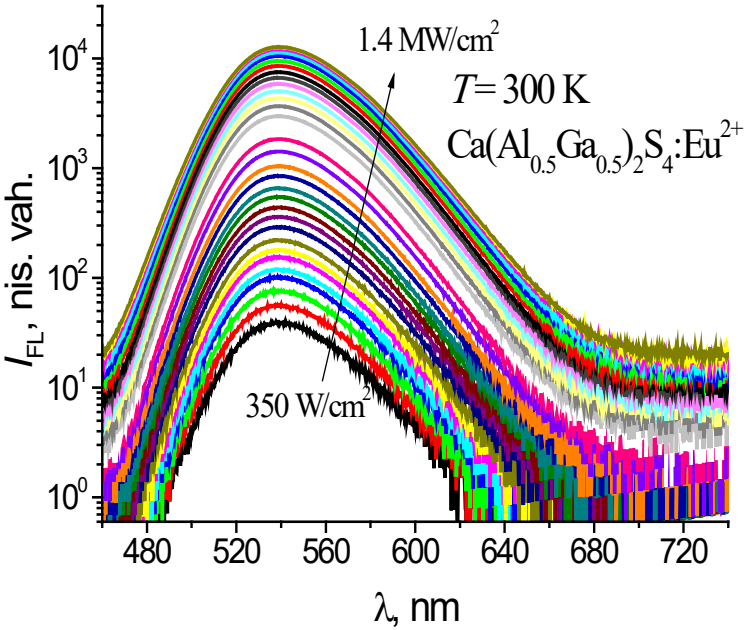

Figure. 2. PL spectra of $Ca(Al_{0.5}Ga_{0.5})_2S_4:Eu^{2+}$solid solutions for different levels of excitation power density (λ=337,1 nm,N_2-laser).

The constant and reducing interval of the PL efficiency (η_{FL}) of $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions were determined depending on the power density of external exciting source at the λ= 337.1 nm (fig. 3). PL efficiency is constant inthe range of $3\cdot10^2 \div 2\cdot10^4$ W/cm^2 power density. An essential droop in emission efficiency occurs at excitation levels higher than $2\cdot10^4$ W/cm^2 and it's continued up to 10^6 W/cm^2. The subsequent reduction of the excitation power density from 10^6 W/cm^2 to 10^2 kW/cm^2 resulted in the recovery of the emission efficiency at the former level, which indicates the absence of any material degradation.

As can be seen from the figure, the temperature does not affect the efficiency of the FL, and the efficiencies are at 20 and 300 K is overlap.

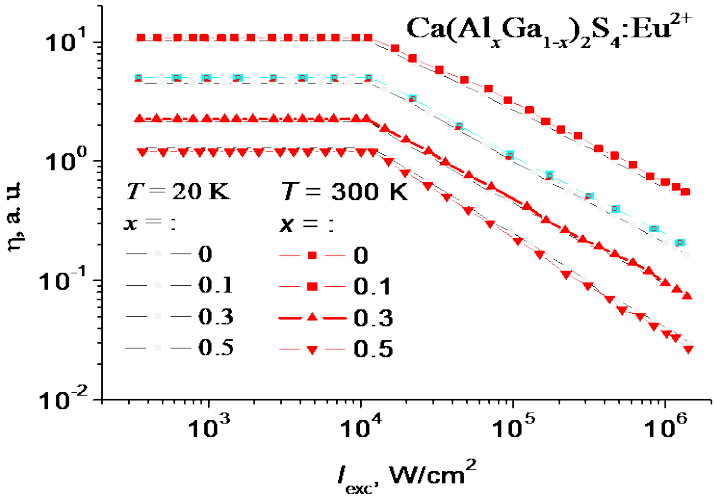

Figure. 3. PL emission efficiency dependences of $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ for x=0; 0,1;0,3;0,5 on the excitation power density at 20 K and 300 K temperatures.

PL kinetics of $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solution for x = 0,5 were measured under the 355 nm of excitation wavelength to clarify the reason for the emission efficiency droop (fig. 4). As can be seen from the figure, the PL decay curves are linear up to $2\cdot10^4$ W/cm^2 power density. PL decay curves at excitation levels below $2\cdot10^4$ W/cm^2 obey monoexponential law (fig. 4, curves 1-4). The PL decay curves change in the shape by increasing in the excitation intensity higher than $2\cdot10^4$ W/cm^2 (fig. 4, curves 5 and 6). This indicates that the additional components with short decay time appeared in the PL kinetics. Obviously, the occurrence of an emission efficiency droop at excitation levels higher than $2\cdot10^4$ W/cm^2 is accompanied by a fast component appearance in the PL decay kinetics of $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions. The main reason for these componentsis that the carriers are absorbed by exciting levels. Thus,the appearance of the short component evidences on the remarkable contribution of the second type quenching in the PL efficiency droop.

The PL kinetics were investigated in case of x = 0 of $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions at different temperatures and lgI ~ t coordinates. PL decay kinetics spectra were measured at 20K,

200K və 300K temperatures using by 10 nsduration of tunable Nd:YAG laser pulsed radiation at 355 nm. The excitation power density was about 3.5 kW/cm^2. It was determined that PL decay parts are linear, i.e. the PL decay obey $I = I_0 \cdot e^{t/\tau}$ exponential law and the time constants change in the range of 463 – 512 ns. It indicated that the PL kinetics of $CaGa_2S_4:Eu^{2+}$ compound weakly depends on temperature.

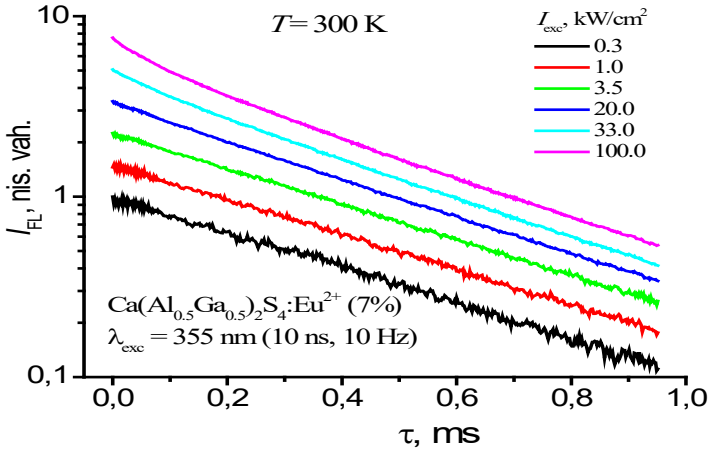

Figure. 4. PL decay kinetics of $Ca(Al_{0,5}Ga_{0,5})_2S_4:Eu^{2+}$solid solutions at 300K temperature.

The PL decay kinetics of $CaGa_2S_4:Eu^{2+}$ compound has been investigated in the range of 20, 200 and 300K temperature, as well as 100 kW/sm^2 of power density. It was observed that the decay curves are not linear at high power densities in all temperatures.This indicates in the formation of fast components along with the slow component of the decay time. Note that the slow component of decay time increase from 435 ns to 489 ns at 100Kw/sm^2 power density by increasing the temperature. The fast component of decay time decreased from 106 ns to 96 ns. Decay time is not monoexponential at high power densities due to the formed additional fast components.The main reason for the fast component formation in the PL kinetics is due to the absorption from excited level.

In chapter IV, the results of the investigations of thermoluminescence properties for $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions are presented in first time. Thermally stimulated luminescence (TL) is one of the best method to investigate trap levels in bandgap of the crystals. The trap levels significantly influence to lifetime of the luminescence. Thus, trap levels occupied carriers and prevent their recombination into the luminescent centers and delay the luminescence.

The TL have studied both doped and undoped samples at the different heating rate and excitation times in the range 80 ÷ 350 K temperature. Obtained TL spectra are wide band and the full width at half maximum and the positions of maximums are changed depending on the heating rate (β). The full width at half maximum changes in the range of 35÷70K when the heating rate change in the range of 0,17 ÷ 1,35 K/s and the maximums of the spectra are shifted to high temperatures.

The TL spectra of the $Ca(Al_xGa_{1-x})_2S_4$ and $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$solid solutions have been studied comparatively. It was determined that the Eu^{2+} ions as an activator in the host matrix have significant effects (both for thermoluminescence curves and peaks positions) in the thermoluminescence properties of $Ca(Al_xGa_{1-x})_2S_4$ solid solutions and cause to observing completely different effects. Thus, the intensities, peaks positions and the number of the peaks of the TL curves changes when Eu^{2+} activator included in the $Ca(Al_xGa_{1-x})_2S_4$ matrix. There are observed two and four maximum respectively in TL spectra of $Ca(Al_xGa_{1-x})_2S_4$ and $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions in case of x = 0.2 and each maximum are suitable to one trap level. If several maximums were observed on the TL spectra, then the traps were distributed at different depths in the bandgap.Less energy is needed to release electrons from shallow traps, but more energy is needed to release electrons from deep traps.

The reason for high TL intensity in the matrix is due to the Eu^{2+} ions are formed new defects at shallow traps.

There are a number of methods and theories for determination the parameters of capture centers. Different parts of the TL curves are using different methods. In some methods are using low-temperature parts or high-temperature parts, but in other methods are

using whole curves and therefore, they have a different precision rate. The following methods were used in the dissertation to the determination of the parameters of trap levels: Lushik method and Urbach method-dropping part of the temperature on the thermoluminescence spectrum are used in these methods and the rate of the kinetics is taken into account when determining the capture center parameters. Note that the value of the rate of kinetics can be one or two. The value of the kinetics rate is the one when the absence of re-absorption of electrons in the traps and is the two when two or more re-absorption of electrons in the traps. The rate of the kinetics of thermoleuminescence process can be determined by theshape the spectrum. The rate of the kinetics is the two when the high temperature part of the spectra is more than low temperature part, otherwise the this value is one.

Randal method and Garlick-Gibson method – the rate of the kinetics is not considered when determining the activation energy of the traps. The activation energy of traps can be determined using Randal's method by knowing the maximum temperature of the thermoluminescence spectrum.

$$E_a = A \cdot k \cdot T_{max}$$

where E_a – activation energy of traps, A – constant, fixed values between 15-30, k – Boltzmann constant ($0.86 \cdot 10^{-4}$ eV), T_{max} – maximum temperature of TL curve.

Activation energy can be determined by the initial point of thermoluminescence intensity using Garlick – Gibson method. It is suggested that at low temperatures the TL intensity varies by $I = I_0 e^{-\frac{E_a}{kT}}$ law, regardless of the rate of kinetics. It has been shown that the intensity of TL linearly depends on the temperature. Activation energy calculated from $\ln I \sim \frac{1}{T}$ dependence. The trap levelparameters of $Ca(Al_xGa_{1-x})_2S_4$ and $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions have been calculated based on these methods. The values of activation energy (E_a), frequency factor (S), capture cross section (S_t) and traps concentrations (N_t)are E_a=0.2 ÷ 0.73 eV , S=$1.1 \cdot 10^8 \div 5 \cdot 10^9$ san^{-1} , S_t= $2.5 \cdot 10^{-19} \div 4 \cdot 10^{-17}$ sm^2, N_t= $1.5 \cdot 10^{16} \div 2 \cdot 10^{17}$ sm^{-3}, respectively.

MAIN RESULT PRESENTED FOR DEFENCE

1. Synthesized $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ ($0 \le x \le 1$) solid solutions exhibit intense photoluminescence due to the electronic transition of Eu^{2+} ions and the change of x appears in the precise tune of the PL band in the range from 560 to 516 nm. It was determined that the centroid shift are decreased by increasing Al^{3+} ions in the $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions. As a result, $5d \rightarrow 4f$ energy transitions increase and the FL spectra shifted towardsshort wavelength.
2. It was determined that the PL integral intensity about 3 times increase in the range 510 – 630 nm wavelength with increasing Eu^{2+} ions concentration from 3% to 7% in the $Ca(Al_xGa_{1-x})_2S_4$ matrix and the shift of the maximums is not observed. The reason for increasing PL integral intensity is due to the equal distribution of Eu^{2+} ions in the crystal and it leads to the reduction of energy transfer between luminescent centers. Non-shifted PL maximum is due to the stable crystal environment around the Eu^{2+} ion.
3. The temperature dependence of PL intensity was studied in the $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$solid solutions.High stability of the integral PL intensity with a drop of only less than35% was revealed in the temperature range from 10 K to 300 K. It is due to the increasing of formed phonons during thethermal vibrations in the crystal lattice.
4. It was shown that the extreme stability of the shape and position of the emission spectra are observed at 20K and 300K temperatures in the range of $3{,}5 \cdot 10^2 \div 1{,}4 \cdot 10^6$ W/cm^2 excitation power density. Moreover, it was determined that the saturating of PL efficiency in the $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ solid solutions are observed only above $2 \cdot 10^4$ W/cm^2.
5. It was determined that the PL kinetics in $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$solid solutions obey exponential law up to $2 \cdot 10^4$ W/cm^2 power density. The shape of the PL decay curves changesat excitation levels higher than $2 \cdot 10^4$ W/cm^2 is accompanied by fast component appearance in the PL decay kinetics which in connection with absorptionfrom excited levels.

6. It was shown that the TL in $Ca(Al_xGa_{1-x})_2S_4:Eu^{2+}$ is due to the electronic traps below 0.2 ÷ 0.7 eV from the bottom of the conduction band and the activation energy (E_a=0,20÷0,73 eV), frequency factor ($S=1{,}1\cdot10^8 \div 5{,}0\cdot10^9$ s^{-1}), concentration ($N_t= 1.5\cdot10^{16} \div 2\cdot10^{17}$ sm^{-3}) and capture cross-section ($S_t= 2{,}5\cdot10^{-19} \div 4\cdot10^{-17}$ sm^2) of electronic traps were determined.

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