

THE INFLUENCE OF EXTERNAL FIELDS ON THE LUMINESCENCE
CHARACTERISTICS OF NANOSTRUCTURE CaGa₂S₄:Eu

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Abstract: The given article is dedicated to the investigation results of photoluminescence (PL) in CaGa₂S₄:Eu nanocrystals excited by ultraviolet (UV), emission of different wavelengths. CaGa₂S₄ compound is obtained in the process of a solid-state chemical reaction. The activation of rare-earth elements (REE) - synthesized compounds is performed between CaS and Ga₂S₃ at a temperature about of 1150°S during the solid-state reaction. According to S.I.Vavilov law, PL energy efficiency in interval 300÷480nm linearly increases when the wavelength of exciting light increases. The maxima at 420, 440, 460, 485nm appear on the excitation spectrum of CaGa₂S₄:Eu²⁺ nanocrystals. The energy of the given excitation light effectively transforms into visible light energy.

Key words: compound, nanocrystal, photoluminescence, nano-crystal surface

1. Introduction

The compounds of CaGa₂S₄ type related to the vast class of high-ohmic ($10^6 \div 10^9$ Ohm) and semiconductors with wide bandgap (4,0÷4,5eV) have general formula II-III₃- VI₄, where II is Pb, Eu, Yb, Ca, Sr, Ba is bivalent cations; III is Ga, In, Al is trivalent cations; VI is S, Se, O, Te is chalcogens. Rare-earth elements (REE) in these materials make efficient emission. [1-4]. Under the influence of these factors, the undoped compounds of CaGa₂S₄ type have the weak structureless emission due to structural defects. Nowadays the investigation connected with the transformation of energy different types into visible light in nanocrystalline semiconductors, in particular, in wide bandgap nano-crystals from a compound of II-III₃-VI₄ group, the striking representative of which is CaGa₂S₄:REE, is of great interest for revealing of physical mechanism, technology, and practical application. The given article is dedicated to investigation results of photoluminescence (PL) in CaGa₂S₄:Eu nanocrystals excited by UV emission of different wavelengths.

2. The synthesis of CaGa₂S₄ compound and sample preparation for PL investigation C.

CaGa₂S₄ compound is prepared in the process of solid-state chemical reaction between CaS and Ga₂S₃ at a temperature about 1150°C. We use two methods to synthesize CaGa₂S₄: 1) CaS and Ga₂S₃ compounds are in evacuated quartz ampoule (10^{-4} millimeter of mercury), the mixture temperature increases up to 1000 reaction continues during 5 hours.; 2) the solid-state reaction between CaS and Ga₂S₃ continues during 4 hours in graphitized quartz crucible under the activated carbon layer at temperature 1000°C. The activation of REE synthesized compounds is carried out during the solid-state reaction. The synthesized compounds in agathic mortar are disintegrated; the obtained powders have the dimensions 5-10µm. Further, these powders are put into a ball mill to disintegrate up to 10-100nm. The luminescent material nanoparticles of CaGa₂S₄:REE is investigated in an atomic force microscope (AFM). As it is known the atomic force microscopy is one of the progressive study methods of nanodimensional materials. Nanocrystals are prepared on surface of polished quartz glass by hand molding method.

AFM scanning from big squares ($60 \times 60 \mu\text{m}^2$) up to small ($500 \times 500 \text{nm}^2$) ones with the aim to choose nanodimensional surface consisted of $\text{CaGa}_2\text{S}_4:\text{REE}$ nanoparticles is carried out several times in spite of the fact that surface has the smooth molded surface at visual inspection.

The scanning is carried out at room temperature under conditions *ex-situ* at the following parameters: the scanning speed is $3 \mu\text{m}/\text{sec}$, the operating scanning area is $527 \times 527 \text{nm}^2$, the scanning pitch is 4nm , the resolution is 128 points, the feedback amplification is 3, the operating point is 0,6. The scanning surface in 2D format is shown in fig. 1. From figures 1 and 2, it is seen that obtained surface has a certain order both on X, Y and Z axes. The order is more visually seen on profilograms of different cross-sections of the given surface shown in fig.3.

From fig.3 one can conclude that the surface consists of molded or bound together clusters $\text{CaGa}_2\text{S}_4:\text{REE}$ with height dimensions not more $\sim 20 \text{nm}$ on the average, the lateral dimensions of which are commensurable with height ones $\sim 20 \text{nm}$. From this, it is followed that $\text{CaGa}_2\text{S}_4:\text{REE}$ nanoparticles obtained in ball mill have the dimension $\sim 20 \text{nm}$ independently on the direction.

The histogram shows that chosen surface irregularity has mainly the dimensions from 20nm up to 55nm in terms of numbers (fig.4).

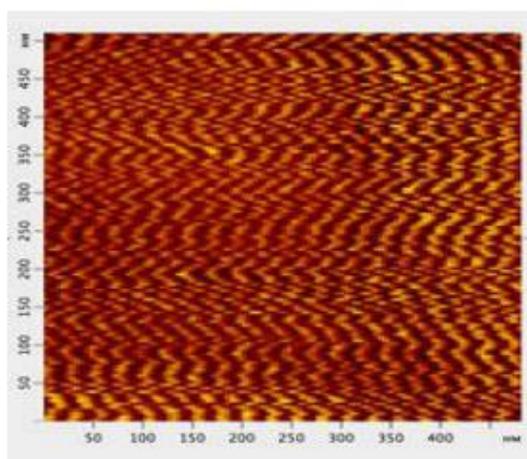


Fig.1. 2D format AFM of CaGa_2S_4 nano-crystal surface after scanning area decrease.

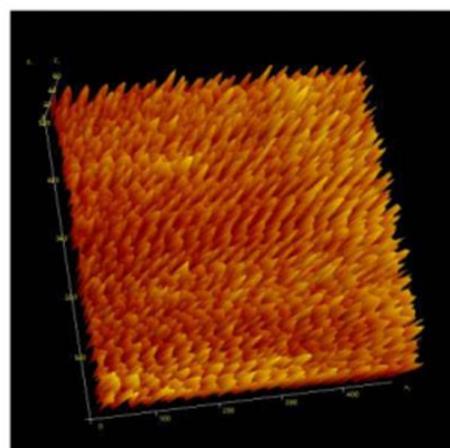


Fig.2. 3D format AFM of CaGa_2S_4 nano-crystal surface of the given surface on fig.1.

3. Measurement results and their discussion

Experimental results show that the $\text{CaGa}_2\text{S}_4:\text{Eu}^{2+}$ polycrystal disintegration leads to weakening of luminescent properties (luminance decrease, loss of luminescent ability, luminescence damping, luminescence color change, and others). However, this fact doesn't influence the use of this compound at the preparation of light sources and a light-emitting diode.

The problem of optical property variations (including luminescent one) of crystal phosphors at their disintegration is analyzed in [5-7]. In these works, it is shown that investigation of obtained nano-dimensional $\text{CaGa}_2\text{S}_4:\text{Eu}^{2+}$ property crystals lead to the conclusion on luminescence molecular nature and luminance decrease is defined by the change of excitation light dispersion. The excitation spectrum representing itself the dependence of luminescence intensity on wavelength or frequency of excitation light takes the important place among spectral characteristics [8,9,13,14].

When the luminescence presents itself the pure intracenter process, emission absorbed by the main lattice can be a non-active one. In our case $\text{CaGa}_2\text{S}_4:\text{Eu}^{2+}$ has weak structureless

luminescence without activator. By excitation spectra one can study the transformation process of light quantum absorbed energy in luminescent emission one [8,13,14].

The excitation and emission spectra of polycrystals (dimensions 10÷100nm) are investigated on spectrofluorimeter "Fluorat-02-Panorama". This spectrofluorimeter allows us to exit the photoluminescence (PL) by different wavelengths in region 200÷690nm. The carried out measurements of PL spectra of nanodimensional powder samples at different excitation light wavelengths give significant information on PL energy efficiency and luminescence spectrum form.

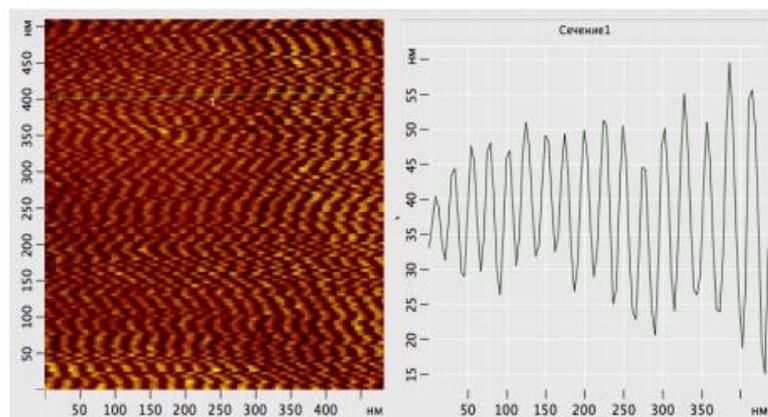
The excitation spectrum of $\text{CaGa}_2\text{S}_4:\text{Eu}^{2+}$ nanocrystals is presented in fig.5. It is seen that maxima at 420, 440, 460 and 485nm appear in the excitation spectrum. The excitation spectra have the wavelength region 360÷520nm. As it is seen from fig.5, PL intensity decreases at 490nm.

$\text{CaGa}_2\text{S}_4:\text{Eu}^{2+}$ PL spectra at different wavelengths of excitation light are shown in fig.6. From this figure one can make the following conclusions: 1) PL spectrum form doesn't depend on excitation light wavelength; 2) PL intensity maxima increase when excitation light wavelengths decrease. The analysis of investigated PL spectra presented in fig.6 shows that Stokes losses $\Delta E = E_{\text{exc}} - E_L$ decrease from 0,54 up to 0,23eV (where E_{exc} is excitation light energy, E_L is energy corresponding to PL spectrum maxima on fig.6). This shows the ex of excitation light the less energy λ more wavelength losses at light transformation in effective luminophores which are $\text{CaGa}_2\text{S}_4:\text{Eu}^{2+}$ compounds. It should be noted that excitation light wavelength doesn't overlap with the emission wavelength of CaGa_2S_4 compound. On the base of data presented in fig.6, one can conclude that PL maxima positions almost don't depend on excitation light wavelength and they correspond to $5d4f \rightarrow {}^8\text{S}_{2/7}$ electron transitions of (Eu^{2+}) europium ions.

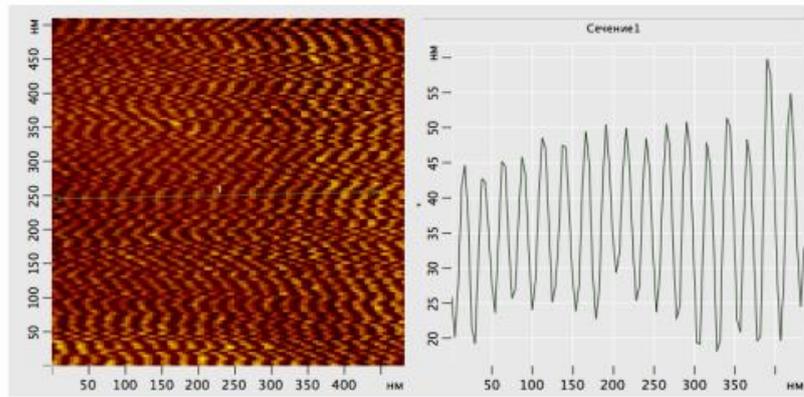
Note that S.I.Vavilov firstly paid attention to the independence of PL spectrum form on excitation light different wavelengths 90 years ago [11,12]. He introduced the perceptions of energy and quantum efficiencies for luminescence characteristics [11,12]. These parameters are analyzed by many authors (see, for example, [10,14,16,17]).

S.I.Vavilov shows that PL energy efficiency in the Stokes region increases proportionally to excitation light wavelength (λ_{exc}) and rapidly decreases in anti-Stokes one up to zero at further λ_{exc} increase. The ratio of energy emitted at PL to absorbed excitation light energy is called by PL energy efficiency (B_e).

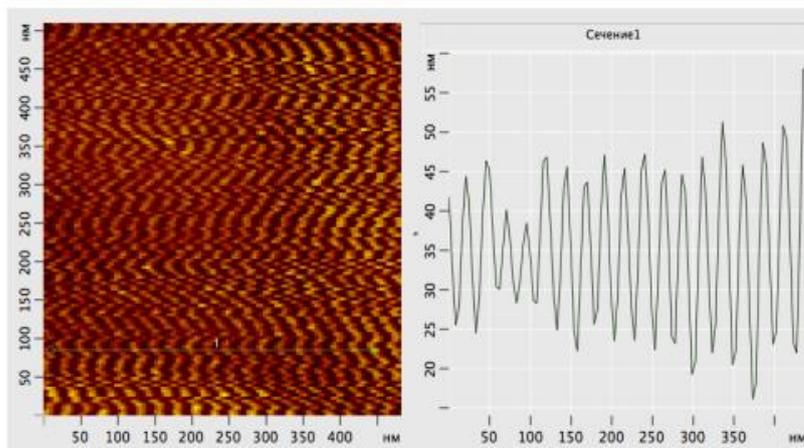
$$B_e = \frac{h\nu_{\text{em}}}{h\nu_{\text{exc}}} B_k = \frac{\lambda_{\text{exc}}}{\lambda_{\text{em}}} B_k \quad (1)$$



a)



b)



c)

Fig.3. The surface profilograms on different sections - a);-b) and -c) from AFM sample in fig.1.

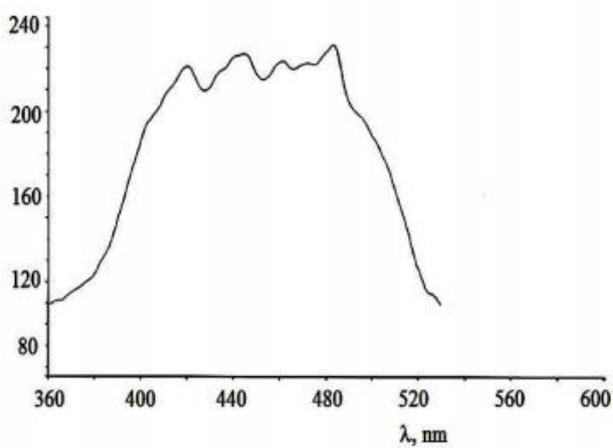


Fig.4. The surface histograms $527 \times 527 \text{ nm}^2$ from fig.1.

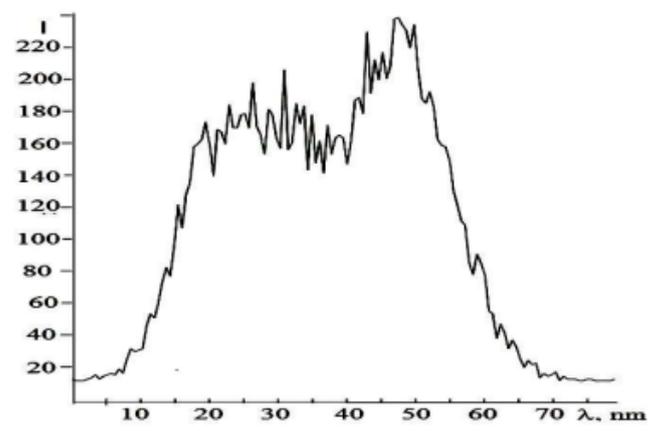


Fig.5. Excitation spectrum $\text{CaGa}_2\text{S}_4 \text{Eu}^{+2}$ at $T=300\text{K}$.

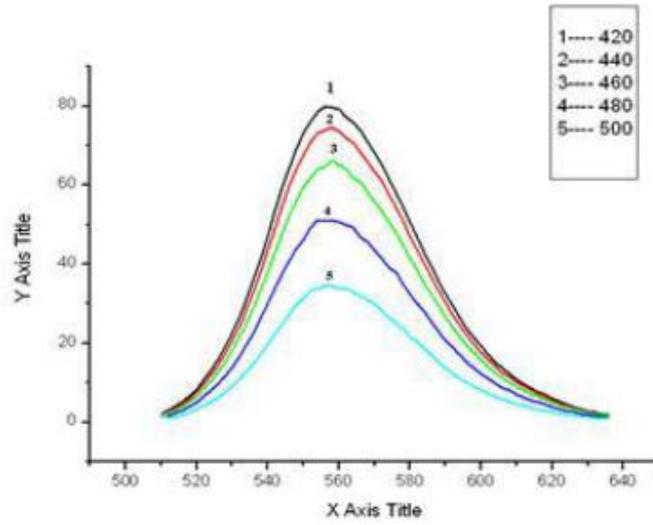


Fig.6. Photoluminescence of $\text{CaGa}_2\text{S}_4 \text{Eu}^{2+}$ nanocrystals at different excitation light wavelengths. $T=300\text{K}$.

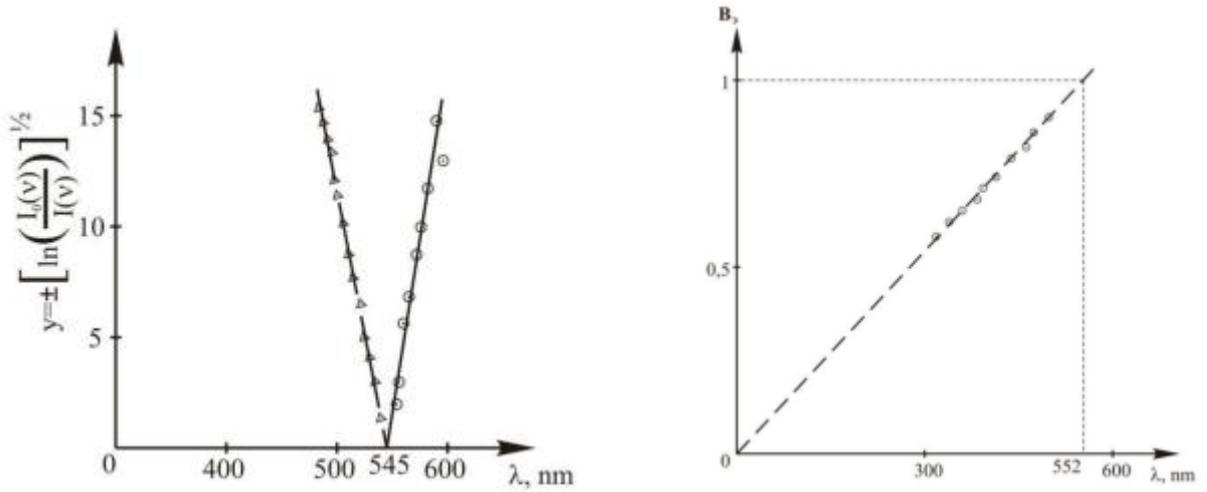


Fig.7. Dependence of energy coefficient B_e on excitation light wavelength

Fig.8 $y = \pm \left[\ln \left(\frac{I_0 v}{I v} \right) \right]^{\frac{1}{2}}$ dependence on light wavelength at which the photoluminescence is observed. $T=300\text{K}$.

Indeed, as it is shown in [17], the expressions for PL energy efficiency when luminescence spectral composition in wide limits independent on wavelength or frequency of excitation light, has the following form:

$$B_e = \frac{h \int \nu W(\nu_{exc}, \nu) d\nu}{h \nu_{exc}} = \frac{\nu}{\nu_{exc}} \quad (2)$$

where ν is frequency average value in luminescence band, where $W(\nu_{exc}, \nu)$ is $h\nu$ quantum emission probability.

When emission probability doesn't depend on excitation light frequency (ν_{exc}) one can write. $W(\nu_{exc}, \nu) = W(\nu)$. In this case $B_e \sim \frac{1}{\nu_{exc}} \sim \lambda_{exc}$ (taking into consideration $\nu = \frac{c}{\lambda_{exc}}$)

and we make the conclusion on linear dependence B_e on λ_{exc} . The expression (2) takes place when luminescence quantum efficiency is equal to the unit: $B_K=1$.

At $B_K \neq 1$ energy efficiency, B_e differs from expression (2) by B_K multiplier for luminescent materials with PL spectra. The processes taking place in luminescent materials are described in detail in [13-17]. The spectrum form and quantum efficiency of luminescence don't depend on excitation light wavelength (Vavilov law). This takes place because of the fact that luminescent emission appears always from lower excited levels irrespective of the fact which activator level was excited after absorption 300 ÷ 480nm [8,10,14].

On the base of experimental data showed on fig.5 PL energy efficiency B_e in nanocrystals $CaGa_2S_4:Eu^{2+}$ is obtained. The results for nanocrystals are shown in fig.6.

According to Vavilov law, this figure shows that linear dependence between B_e and λ_{exc} exists in 320 ÷ 480nm region. As Vavilov mentioned, the dependence between B_e and λ_{exc} leads to simple empirical law $B_e = k\lambda_{exc}$ where k is a constant value, λ_{exc} is excitation light wavelength. Constant k is PL quantum efficiency: $B_K = k$. Fig.6 shows that extrapolation of dependence $B_e = f(\lambda_{exc})$ has the region for B_e from 0 up to 1. As it is above mentioned, experimental results for B_e and B_K are between 320 and 480nm. At the same time, the emission intensity strongly decreases that corresponds to excitation light wavelength above 480nm. The theoretical trend of curve $B_e = f(\lambda_{exc})$ is shown in fig.6 by dotted line. The extrapolation line $B_e = f(\lambda_{exc})$ to increase of λ_{exc} value crosses B_e axis in A point with coordinates (1 and 500nm). This confirms S.I.Vavilov's idea on the fact that PL energy efficiency can't be more than unity: $B_e=1$.

In temperature interval 10 ÷ 350K the measurement of PL spectrum full width at half maximum (FWHM) in Eu,Ca,Ba tiogallats shows that Huan Rice parameter S changes from 5 up to 10 [1-4]. This shows that in given materials the electrophonon interaction takes place and PL spectral dependence is described by Gaussian distribution [19].

$$I(h\nu) = \frac{1}{\sigma(2\pi)^2} \exp\left[-\frac{(h\nu - h\nu_0)^2}{2\sigma^2}\right] \quad (3)$$

where $h\nu$ is excitation emission energy; $h\nu_0$ is photon energy corresponding to the maximum in PL spectrum, σ is constantly connected with squared half-width $W(T)$ by the following expression:

$$W(T)^2 = \sigma^2 8 \ln 2 \quad (4)$$

According to Gaussian distribution the experimental data represented for PL spectrum of $CaGa_2S_4:Eu^{2+}$ nanocrystal samples in $y = f(h\nu)$ coordinates have the form of the line (fig.7) where

$$y = \pm \left[\ln \left(\frac{I_0(\nu)}{I(\nu)} \right) \right]^{1/2}. \text{ The correspondence of PL spectrum to Gaussian distribution allows us to}$$

define the energy position of intensity maximum and PL spectrum half-width with accuracy.

4. Conclusion

The excitation and emission spectra of nanodimensional crystals and volume crystals $\text{Ga}_2\text{S}_4:\text{Eu}^{2+}$ are investigated at temperatures 77 and 300K. According to S.I.Vavilov law, it is shown that PL energy efficiency in interval 300÷480nm linearly increases when the excitation light wavelength increases. The maxima at 420, 440, 460, 485nm of wavelengths are revealed on the excitation spectrum of $\text{CaGa}_2\text{S}_4:\text{Eu}^{2+}$ nanocrystals. The energy of given excitation light wavelengths effectively transforms into visible light energy.

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ВЛИЯНИЕ ВНЕШНИХ ПОЛЕЙ НА ЛЮМИНЕСЦЕННЫЕ ХАРАКТЕРИСТИКИ НАНОСТРУКТУРЫ $\text{CaGa}_2\text{S}_4:\text{Eu}$

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Резюме: Данная статья посвящена результатам исследования фотолюминесценции (ФЛ) в нанокристаллах $\text{CaGa}_2\text{S}_4:\text{Eu}$, возбуждаемых ультрафиолетом (УФ), излучением разных длин волн. Соединение CaGa_2S_4 получают в процессе твердофазной химической реакции. Активация соединений, синтезированных редкоземельными элементами (РЗЭ), проводится между CaS и Ga_2S_3 при температуре около 1150°C во время твердофазной реакции. Согласно закону С.И.Вавилова, эффективность энергии ФЛ в интервале 300 ÷ 480нм линейно возрастает при увеличении длины волны возбуждающего света. Максимумы при 420, 440, 460, 485 нм

проявляются в спектре возбуждения нанокристаллов $\text{CaGa}_2\text{S}_4:\text{Eu}^{2+}$. Энергия данного возбуждающего света эффективно превращается в энергию видимого света.

Ключевые слова: соединение, нанокристалл, фотолюминесценция, нанокристаллическая поверхность.

CaGa_2S_4 NANOSTRUKTURLARININ LÜMINİSENSSIYA XASSƏLƏRİNƏ XARİCİ SAHƏLƏRİN TƏSİRİ

R.A. Abdulheyov

Xülasə: Verilən məqalə müxtəlif dalğa uzunluqlu ultrabənövşəyi (UB) şüalar ilə həyəcanlanan $\text{CaGa}_2\text{S}_4:\text{Eu}$ nanokristalında fotolüminessensiyanın (PL) tədqiqinə həsr olunmuşdur. CaGa_2S_4 birləşməsi bərkfazlı kimyəvi reaksiya prosesində hazırlanır. Nadir torpaq elementlərinin (REE) - sintez olunmuş birləşmələrin aktivləşməsi qatı reaksiya zamanı təxminən 1150° temperaturda CaS və Ga_2S_3 arasında aparılır. S.I.Vavilov qanununa görə, həyəcanlanan işığın dalğa uzunluğu artdıqda, $300 \div 480\text{nm}$ intervalında FL enerjinin effektivliyi xətti olaraq artır. $\text{CaGa}_2\text{S}_4:\text{Eu}^{2+}$ nanokristalların həyəcan spektrində maksimum 420, 440, 460, 485 nm dalğa uzunluqlarında aşkar edilmişdir. Həyəcanlanan işığın dalğa uzunluqlarının enerjisi effektiv görünən işıq enerjisinə çevrilir.

Açar sözlər: birləşmə, nanokristal, fotolüminessensiya, nano-kristal səth