

LIGHT TRANSFORMATION OF DIFFERENT LENGTH WAVES IN NANO-CRYSTALS OF ALKALINE-EARTH COMPOUNDS OF CaGa_2S_4 TYPE

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The given article is dedicated to investigation results of photoluminescence (PL) in CaGa_2S_4 :Eu nanocrystals excited by ultraviolet (UV), emission of different wavelengths. CaGa_2S_4 compound is prepared in the process of solid-state chemical reaction between CaS and Ga_2S_3 at temperature about 1150° C. The activation of rare earth elements (REE) - synthesized compounds is carried out during solid-state reaction. 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 excitation spectrum of CaGa_2S_4 :Eu²⁺ nanocrystals. The energy of given excitation light wavelengths effectively transforms into visible light energy.

Keywords: photoluminescence, nanocrystals, rare earth elements, compounds.

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INTRODUCTION

The compounds of CaGa_2S_4 type relate to vast class of high-ohmic ($10^6 \div 10^9 \text{ Ohm}\cdot\text{m}$) and wide bandgap semiconductors (4,0-4,5eV) having general formula II-III₃-VI₄, where II are Pb, Eu, Yb, Ca, Sr, Ba bivalent cations; III are Ga, In, Al trivalent cations; VI are S, Se, O, Te chalcogens.

Rare-earth elements (REE) in these materials make efficient emission centers [1-4].

The triple compounds of CaGa_2S_4 :REE type are perspective materials to transform of electric field energy, ultraviolet (UV), infrared (IR) [1-4] and X-ray emissions and also α , γ particle energies into visible light energy. Under influence of these factors, the undoped compounds of CaGa_2S_4 type have the weak structureless emission due to structural defects.

Nowadays the investigation connected with transformation of energy different types into visible light in nanocrystalline semiconductors, in particular, in wide bandgap nano-crystals from compound of II-III₃-VI₄ group, the striking representative of which is CaGa_2S_4 :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 CaGa_2S_4 :Eu nanocrystals excited by UV emission of different wavelengths.

THE SYNTHESIS OF CaGa_2S_4 COMPOUND AND SAMPLE PREPARATION FOR PL INVESTIGATION

CaGa_2S_4 compound is prepared in the process of solid-state chemical reaction between CaS and Ga_2S_3 at temperature about 1150° C. We use the two methods of CaGa_2S_4 synthesis: 1) CaS and Ga_2S_3 compounds are in evacuated quartz ampoule (10^{-4} millimeter of mercury), the mixture temperature increases up to 1000°C and the

reaction continues during 5 hours.; 2) the solid-state reaction between CaS and Ga_2S_3 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 solid-state reaction.

The synthesized compounds in agathic mortar are disintegrated; the obtained powders have the dimensions 5-10 μm . Further, these powders are put into ball mill to desintegrate up to 10-100nm.

The luminescent material nano-particles of CaGa_2S_4 :REE are investigated in atomic force microscope (AFM). As it is known the atomic force microscopy is the 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 (60x60 μm^2) up to small (500x500 nm^2) ones with the aim to choice nanodimensional surface consisted of CaGa_2S_4 :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 following parameters: the scanning speed is 3 $\mu\text{m}/\text{sec}$, operating scanning area is 527x527 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 on fig.1. From figures 1 and 2 it is seen that obtained surface has the certain order both on X, Y and Z axes. The order is more visually seen on profillograms of different cross sections of given surface shown on fig.3.

From fig.3 one can conclude that the surface consist of molded or bound together clusters CaGa_2S_4 :REE with height dimensions not more ~20nm on the average, the lateral dimensions of which are commensurable with height ones ~20nm. From this it is followed that CaGa_2S_4 :REE nanoparticles obtained in ball mill have the dimension ~20nm independently on direction.

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

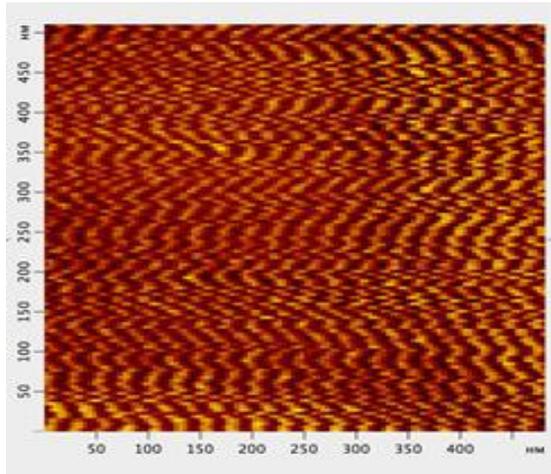


Fig.1. 2D format AFM of CaGa₂S₄ nano-crystal surface after scanning area decrease.

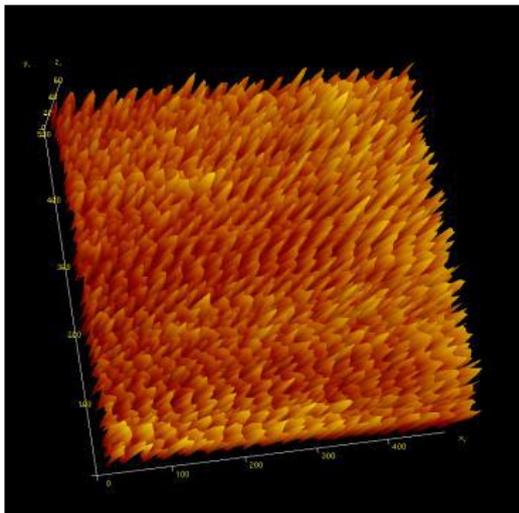


Fig.2. 3D format AFM of CaGa₂S₄ nano-crystal surface of the given surface on fig.1.

MEASUREMENT RESULTS AND THEIR DISCUSSION.

Experimental results show that the CaGa₂S₄:Eu²⁺ poly crystal 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 on use of this compound at preparation of light sources and 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 CaGa₂S₄:Eu²⁺ property crystals leads to the conclusion on luminescence molecular nature and luminance decrease is defined by change of excitation light dispersion. The excitation spectrum representing itself the dependence of lu-

minescence 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 main lattice can be non-active one. In our case CaGa₂S₄:Eu²⁺ has the 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 excite 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 gives the significant information on PL energy efficiency and luminescence spectrum form.

The excitation spectrum of CaGa₂S₄:Eu²⁺ nanocrystals is presented on fig.5. It is seen that maxima at 420, 440, 460 and 485nm appear in excitation spectrum. The excitation spectra have the wavelength region 360÷520nm. As it is seen from fig.5, PL intensity decreases at 490nm.

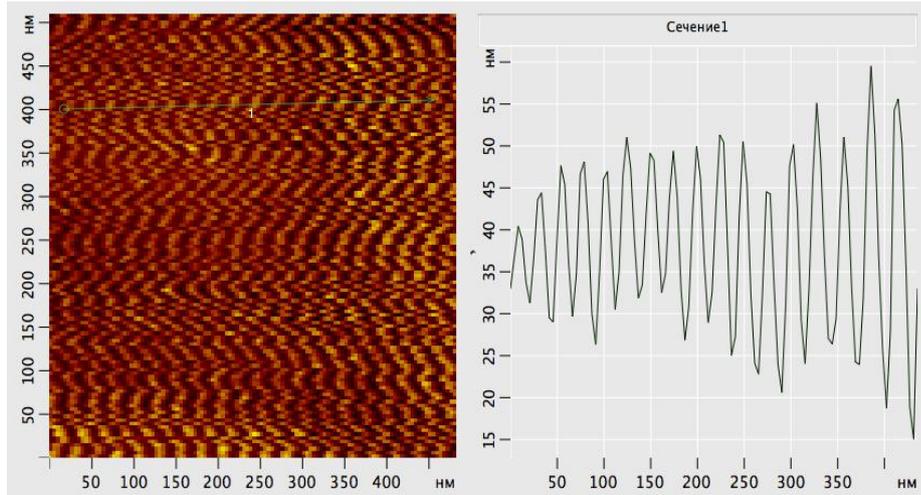
CaGa₂S₄:Eu²⁺ PL spectra at different wavelengths of excitation light are shown on fig.6. From this figure one can make the following conclusions: 1) PL spectrum form doesn't depend on excitation light wavelength; 2) PL intensity maxima increase when excitation light wavelengths decrease. The analysis of investigated PL spectra presented in fig.6, shows that Stokes losses $\Delta E = E_{exc} - E_L$ 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 more wavelength λ_{exc} of excitation light the less energy losses at light transformation in effective luminophors which are CaGa₂S₄:Eu²⁺ compounds. It should be noted that excitation light wavelength doesn't overlap with emission wavelength of CaGa₂S₄ 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 $5d4f \rightarrow {}^8S_{7/2}$ electron transitions of (Eu²⁺) europium ions.

Note that S.I.Vavilov firstly paid attention on 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 analysed by many authors (see for example, [10,14,16,17]).

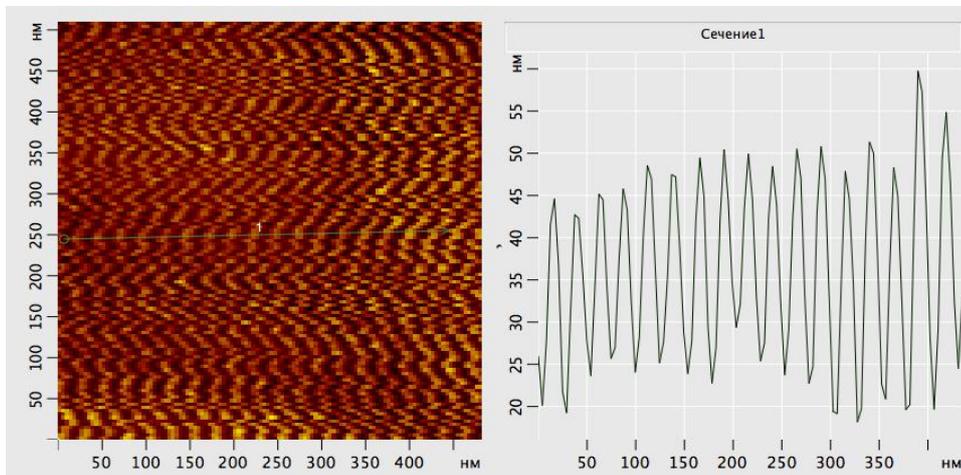
S.I.Vavilov shows that PL energy efficiency in Stokes region increases proportionally to excitation light wavelength (λ_{exc}) and rapidly decreases in anti-Stokes one up to zero at further λ_{exc} increase.

The ratio of energy emitted at PL to absorbed excitation light energy is called by PL energy efficiency (B_e).

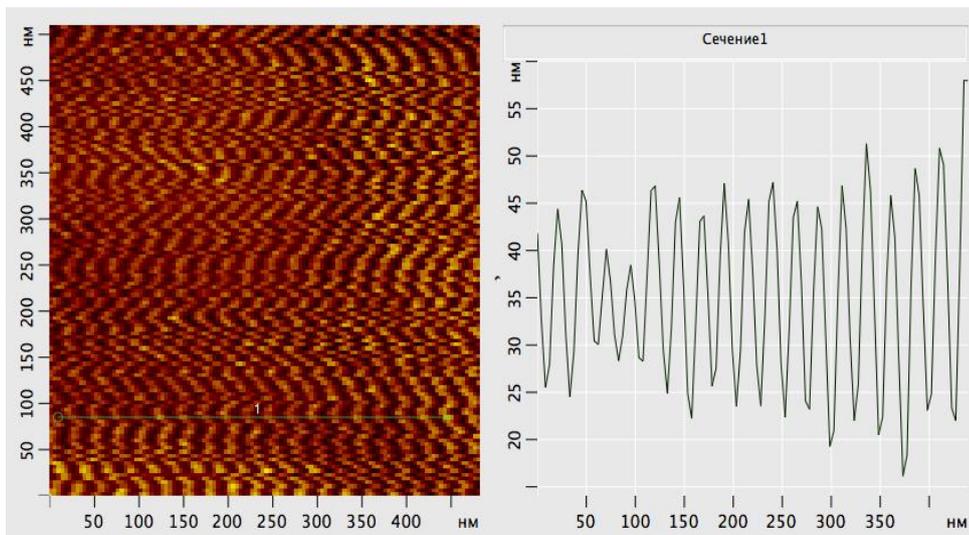
$$B_e = \frac{h\nu_{em}}{h\nu_{exc}} B_k = \frac{\lambda_{exc}}{\lambda_{em}} B_k \quad (1)$$



a)



b)



c)

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

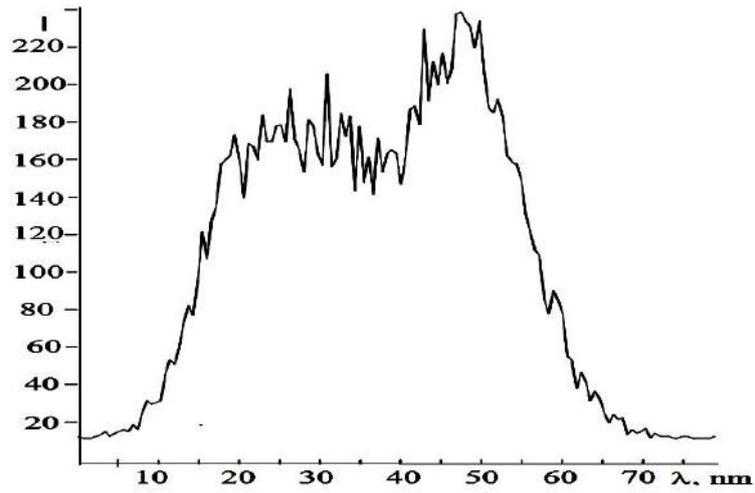


Fig.4. The surface histograms 527x527nm² from fig.1.

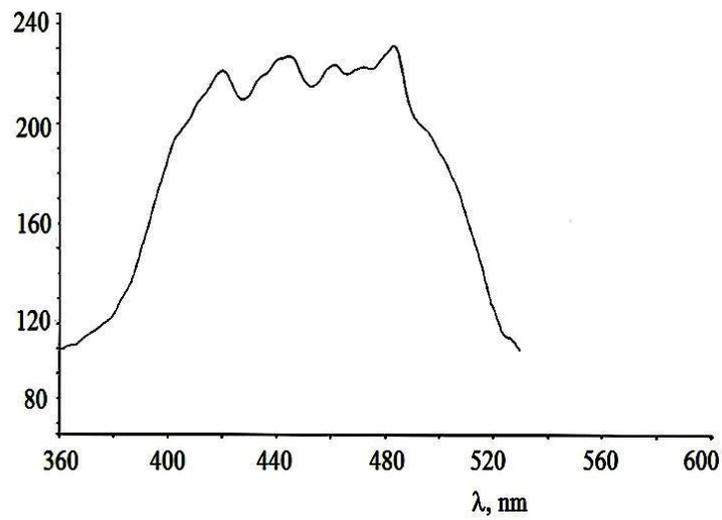


Fig.5. Excitation spectrum CaGa₂S₄ Eu⁺² at T=300K.

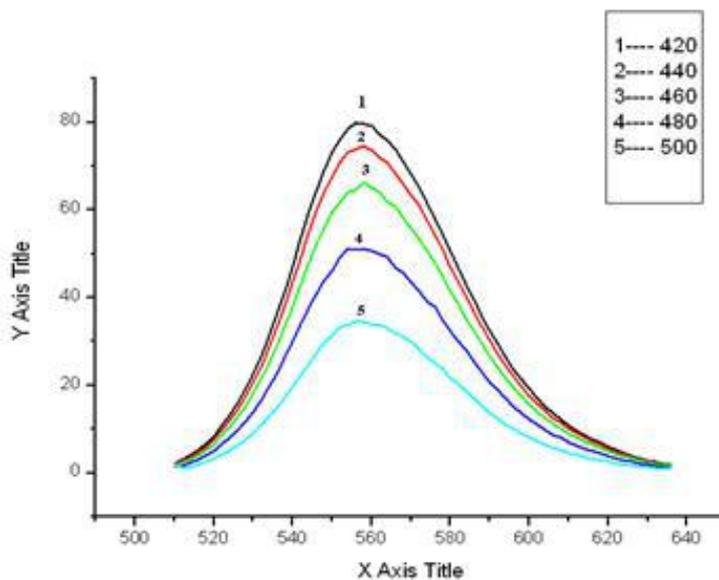


Fig.6. Photoluminescence of CaGa₂S₄ Eu⁺² nanocrystals at different excitation light wave lengths. T=300 K.

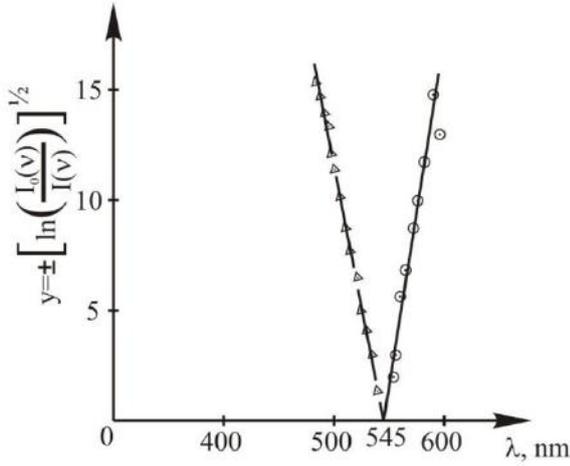


Fig.7. Dependence of energy coefficient B_e on excitation light wavelength.

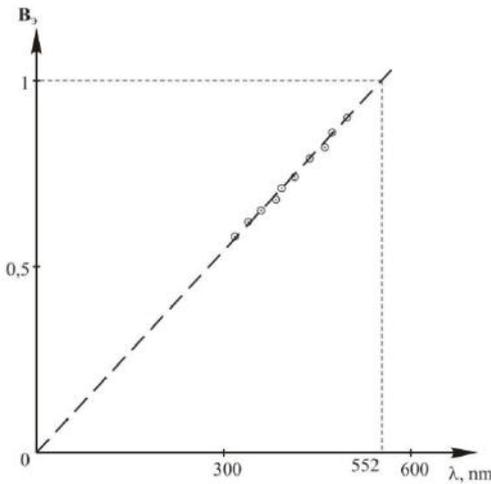


Fig.8 $y = \pm \left[\ln \left(\frac{I_0 v}{I v} \right) \right]^{1/2}$ dependence on light wavelength at which the photoluminescence is observed. $T=300K$.

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, $W(\nu_{exc}, \nu)$ 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 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 details 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 level irrespective of the fact which activator level was excited after absorption 300÷480nm [8,10,14].

On the base of experimental data shown on fig.5 PL energy efficiency B_e in nanocrystals $CaGa_2S_4:Eu^{2+}$ is obtained. The results for nanocrystals are shown on 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 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 on 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 maximum in PL spectrum, σ is constant connected with squared half-width $W(T)$ by 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 line (fig.7) where $y = \pm \left[\ln \left(\frac{I_0(v)}{I(v)} \right) \right]^{1/2}$. 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.

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 in-

creases when the excitation light wavelength increases. The maxima at 420, 440, 460, 485nm of wavelengths are revealed on 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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