# PHOTOLUMINESCENCE OF $CaGa_2S_4$: REE (REE-Eu, Er, Nd, Pr)

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This article presents the results of studies of the photoluminescent properties of CaGa2S4 crystal activated by rare earth ions Eu, Er, Pr, and Nd. It has been established that europium-activated calcium thiogallates are more promising materials as luminophores than similar selenogallates, since they demonstrate greater efficiency and stability of PL and can be used in LEDs, lasers and displays. In telecommunication band C (1530-1560 nm), Er-doped thiogallate exhibits a strong luminescence with a decay time of the order of 2.7 ms promising for laser applications. The use of Nd as the activator is caused by the fact that element in different amorphous and crystal matrixes forms the radiation centers in visible (400-700nm) and nearest IR (900 – 1400nm) fields of electromagnetic spectra.

**Keywords:** rare earth ion, wavelength, emission spectrum, excitation spectrum

## INTRODUCTION

Doping of various materials with rare-earth elements (REE) allows to enhance the quantum yield of their luminescence due to the formation of the emitting centers in which the effective energy transfer from the excited charge carriers to 4f-electrons takes place. It also allows to determine the electron transitions responsible for the emission bands. In this respect semiconductor alkaline-earth chalcogenides II–$III_2$–$VI_4$, including $CaGa_2S_4$, seem to the most promising. As compared to its binary analog, $CaGa_2S_4$ has a low melting temperature (less than 1500 K), features a higher degree of covalent bounding, the compound is moisture - resistant and requires approximately half as much energy for luminescence excitation. Because the ionic radii of the REE and Ca differ little, $CaGa_2S_4$ can be strongly doped with REE (up to $10^{21}$ $cm^{-3}$). $CaGa_2S_4$ compound belongs to the group of triple chalcogenides with general formula of II-$III_2$-$VI_4$ (where II are Ba, Sr, Ca, Eu bivalent cations; $III_2$ are Ga, In, Al trivalent cations; $VI_4$ are S, Se, Te chalcogens) which has the series of advantages in comparison with double analogues (for example, CaS, BaS, EuS). The combination of profitable properties such as low melting temperature (1100 - 1500K), stability to different solvents, to moisture and other external factors give us the possibility of wide use of this compound in scientific and practical aims. Calcium thiogallate ($CaGa_2S_4$) doped with REE is a prospective material for optoelectronic and photonic applications [1]. Maximum phonon energy and good optical transmission properties allows to the realization of high-efficiency phosphors [2, 3], whose good electrical conduction properties are also promising for electroluminescent displays [4]. $CaGa_2S_4$ doped with erbium exhibits a photoluminescence (PL) emission at 1554nm, suitable for telecommunication application in the C band [5] while doping with Dy and Nd was investigated for laser applications [6, 7]. Calcium thiogallate crystallizes in an orthorhombic structure with space group $D_{2h}^{24}$–Fddd [8] and is characterized by three different crystallographic sites for the calcium ion: two with $D_2$ point symmetry and one with $C_2$.

## MEASUREMENTS

This paper describes the results obtained for $CaGa_2S_4$: REE polycrystals prepared by solid-phase synthesis from stoichiometric amounts of calcium ~CaS: 99.99! and gallium ($Ga_2S_3$: 99.95) sulfide powders in a sulfur vapor atmosphere at 1000°C in a vacuum of $10^{-4}$ Torr during 4 h., Upon completion of the synthesis, four-hour annealing was performed at 700°C in the atmosphere of argon with hydrogen sulfide pumped sealed quartz bulb. Activation by REE (Eu, Er, Pr, Nd) was realized using $REEF_3$ ~99.9 doping during the synthesis process.

## EXPERIMENTAL RESULTS

The $Eu^{2+}$ ion is known to emit luminescence during the f→d transition. The energy position of this emission depends on the host material and changes from the near-UV region to the visible red region of the spectrum. As the crystal field strength increases, the position of the emission maximum shifts toward longer wavelengths. The PL excitation spectrum of $CaGa_2S_4$:$Eu^{2+}$ is an extremely broad band that overlaps with the emission spectrum over a wide range of the visible region (Fig. 1). The observed excitation spectrum is explained by the absorption of $Eu^{2+}$ ions, since the unactivated $CaGa_2S_4$ compound does not absorb in this spectral region. The emission spectrum is a band with a maximum at 2.21 eV and a half-width of 0.23 eV at 300 K. In this case, the transition occurs from the lower excited level $4f^65d$ to the ground $4f^7$ ($^8S7/2$) level [9].

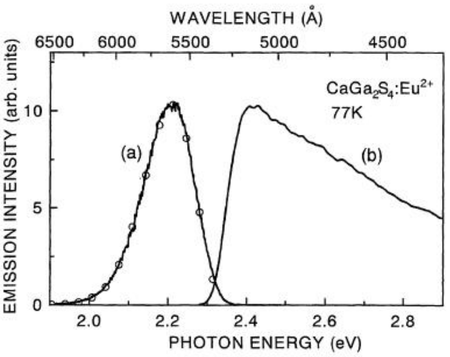

*Fig.1.* Emission (a) and excitation (b) spectra in $CaGa_2S_4:Eu^{2+}$ single crystals at 77 K.

The $CaGa_2S_4$:Er emission spectra at room and liquid nitrogen temperatures obtained under $l_{exc} = 337.1$ nm in this charge transfer band are presented on Fig.2. In the range 370 to 700 nm, these spectral lines were already attributed mainly to transitions from the $^4G_{11/2}$, $^2H_{9/2}$, $^4F_{3/2}$, $^4F_{5/2}$, $^4F_{7/2}$, $^2H_{11/2}$, and $^4S_{3/2}$ states to $^4I_{13/2}$ and $^4I_{15/2}$ $Er^{3+}$ ion states. The emissions at about 820, 860, and 980 nm can correspond for each one to a superposition of several transitions ~ Fig.3. The $Er^{3+}$ ion states split into many levels due to the spinorbital interaction and crystal field of the $CaGa_2S_4$ host lattice. This splitting gives rise to fine structure of the luminescence. For all these spectral series there was practically no thermal quenching up to room temperature, only changing of the relative intensities of the sharp lines in each series was observed. The influence of these two kinds of centers was analyzed for the up-conversion process. Under an excitation wavelength around 985 nm, we can excite the $^4F_{11/2}$ level with a two-phonon process with the participation of the $^4I_{11/2}$ level energy-state absorption ~ESA and an up-conversion emission is observed in the visible range. In addition to the slight $^4F_{7/2}$ - $^4I_{15/2}$ emission, a strong $^4S_{3/2}$ - $^4I_{15/2}$ emission is observed (Fig. 4.). The different relative intensities of these emission lines can be explained by the mismatching overlap of the energy levels for the two $Er^{3+}$ centers [10].

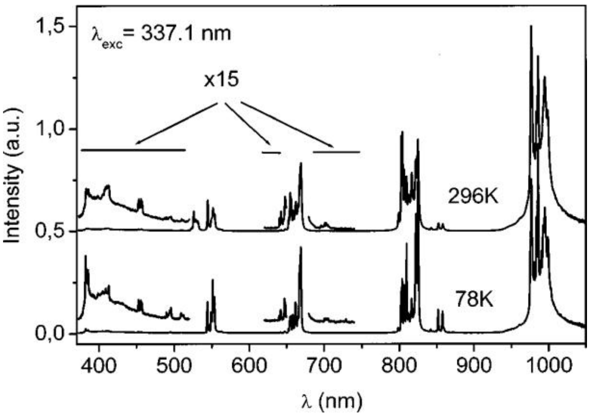

*Fig.2.* Emission spectra of $CaGa_2S_4$ :Er by charge transfer states 337.1 nm excitation at 78 and 296 K in the visible and near IR spectral ranges.

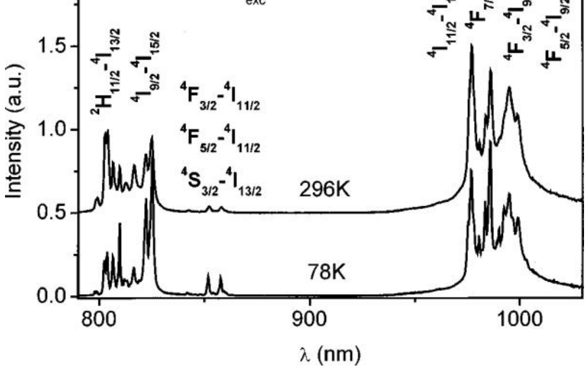

*Fig.3.* Emission spectra of $CaGa_2S_4$ :Er by charge transfer states 337.1 nm excitation at 78 and 296 K in the near IR spectral region.

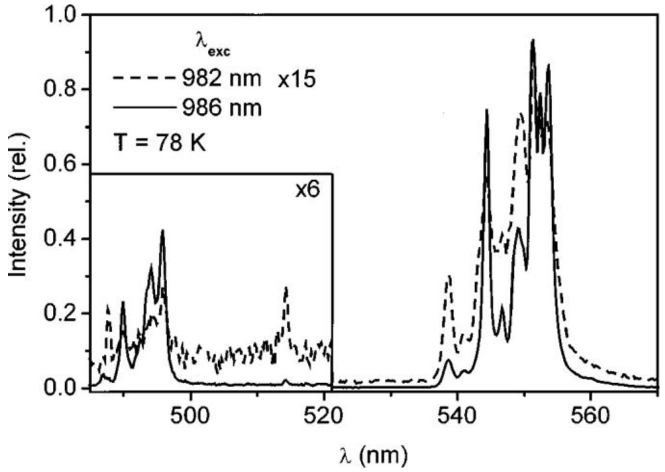

*Fig.4.* Up-conversion emission spectra of $CaGa_2S_4$ :Er under selective excitation: 982 and 986 nm at 78 K.

FL spectra $CaGa_2S_4:Nd^{3+}$ taken at room temperature at light excitation by wave length 325 nm at neodymium different concentrations (1- 5%) are shown in fig.5. It is seen that radiation spectrum covers the wave length range 550 –1200 nm and consists of intracenter luminescence line spectra of $Nd^{+3}$ ion with maxima at wave lengths 596, 670, 808, 878, 901,915, 1064 and 1076 nm connected with $^2G_{7/2}\rightarrow{}^4I_{9/2}$, $^2G_{5/2}\rightarrow{}^4I_{9/2}$, $^2H_{11/2}\rightarrow{}^4I_{9/2}$, $^4F1_{9/2}\rightarrow{}^4I_{9/2}$ and $^2H_{9/2}\rightarrow{}^4I_{9/2}$ transitions. It is shown that observable FL maxima practically don't depend on wave length whereas the radiation intensity in visible spectrum decreases that authenticates the presence of luminescence concentration quenching in the sample with neodymium concentration increasing. Further, the significant increase of FL intensity takes place because of the increase of $Nd^{3+}$concentration in the sample. Thus, one can conclude from analysis of obtained spectra that there are nonequivalent uminescence centers in this compound differing on the intensity /11/.

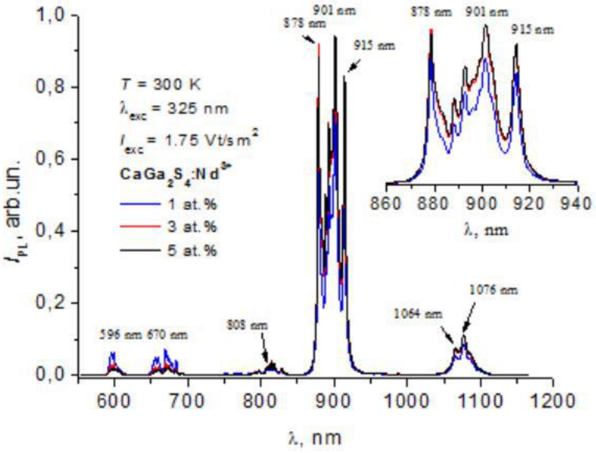

*Fig. 5.* FL spectra $CaGa_2S_4:Nd^{3+}$ at room temperature.

Activation of the $CaGa_2S_4$compound with praseodymium ions with a mass fraction of 3 and 7 at. % leads to the appearance of FL in the wavelength range of 470–760 nm, characterized by a set of lines, the most intense of which are located at 494, 631, 654 and 741 nm and, therefore, are due to the luminescence of $Pr^{3+}$ ions (Fig. 6). The 494 nm PL excitation spectra of $CaGa_2S_4:Pr^{3+}$ at 300 K exhibit a broad band in the 260–360 nm range, peaking at approximately 325 nm. A strong narrow line is present at 456 nm (Fig. 6, inset, transition 1'). The band in the FLE spectra at approximately 325 nm is typical in shape and position for undoped calcium thiogallate. Excitation to this band results in a weak emission in the green region of the spectrum. Consequently, in the PLE spectra of the praseodymium-activated $CaGa_2S_4$ compound, this band is due to the absorption of pump radiation by the calcium thiogallate semiconductor matrix and the subsequent transfer of excitation energy to the praseodymium ions. The maximum in the photoluminescence excitation (FL) spectra of $CaGa_2S_4:Pr^{3+}$ recorded at 494 nm, occurs at a wavelength of 456 nm. With an increase in the $Pr^{3+}$ ion concentration to 7 at.%, the intensity of the 456 nm line in the FL spectra increases relative to the excitation intensity at 325 nm, leading to more efficient FL excitation through transitions in $Pr^{3+}$ ions. In calcium thiogallate, the PL line spectrum of $CaGa_2S_4:Pr^{3+}$ in the wavelength range of 470–760 nm can be associated with electronic transitions in the $Pr^{3+}$ ion, a detailed diagram of which is shown in the inset of Fig. 6. Absorption at a wavelength of 456 nm (transition 1′)

corresponds to direct excitation of carriers from the $^3H_4$ level to the $^3P_2$ level of $Pr^{3+}$ ions, followed by nonradiative relaxation to the $^3P_1$, $^3P_0$, and 1D2 levels. Electronic transitions from the $^3P_0$ level to $^3H_4$, $^3H_6$, $^3F_2$, and $^3F_4$ form a group of the most intense lines in the FL spectrum of the $CaGa_2S_4$:$Pr^{3+}$ compound at wavelengths of 494 nm (1), 631 nm (4), 654 nm (5), and 741 nm (7), respectively. An order of magnitude weaker emission at wavelengths of 537 nm (2) and 688 nm (6) is due to transitions from the $^3P_1$ level to $^3H_5$ and $^3F_3$, respectively, and at 611 nm (3) to the $^1D_2$ $^3H_4$ transition. The luminescence intensity due to the $^1D_2 \rightarrow$ $^3H_4$ electron transition is subject to concentration quenching with an increase in the proportion of praseodymium ions in $CaGa_2S_4$ from 3 to 7 at.%. An increase in the proportion of praseodymium ions in $CaGa_2S_4$ from 3 to 7 at.% leads to a twofold increase in the integrated PL intensity, with the exception of a 10% drop in the luminescence intensity in the vicinity of 611 nm /12/.

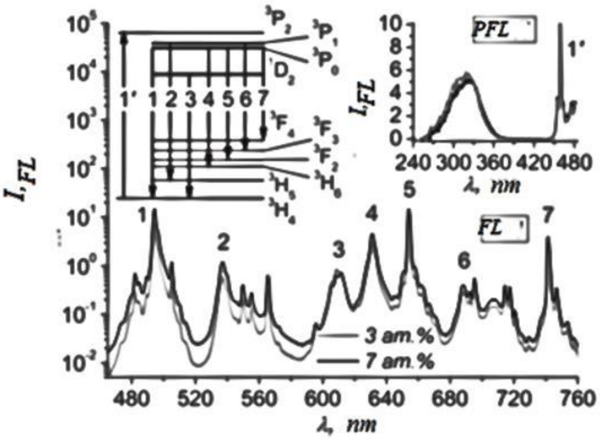

*Fig. 6.* FL spectra of $CaGa_2S_4$:$Pr^{3+}$ at 300 K and excitation at 456 nm for two $Pr^{3+}$ ion concentrations: 3 and 7 at.%. The inset shows a diagram of the electronic transitions in $Pr^{3+}$ ions on the left (the numbers indicate the transitions corresponding to the lines in the FL and FLE spectra); on the right are the PLE spectra at 300 K and recorded at 494 nm (normalized to intensity at 456 nm).

## CONCLUSION

It has been established that europium-activated calcium thiogallates are more promising materials as luminophores than similar selenogallates, since they demonstrate greater efficiency and stability of PL and can be used in LEDs, lasers and displays. The investigation of the visible and near IR emission of $CaGa_2S_4$:Er polycrystals demonstrates the presence of two different types of Er centers in connection with the crystal structure of the ternary compound host matrix. In telecommunication band C (1530-1560 nm), Er-doped thiogallate exhibits a strong luminescence with a decay time of the order of 2.7 ms promising for laser applications. The previous investigations show that $CaGa_2S_4$ is effective matrix for many rare-earth ions, in particular, for neodymium ions that allow us to effectively transform the energy of electric field, electron beams, ultraviolet radiations and etc into visible light. The use of Nd as the activator is caused by the fact that element in different amorphous and crystal matrixes forms the radiation centers in visible (400-700nm) and nearest IR (900 – 1400nm) fields of electromagnetic spectra. It was found that increasing the proportion of praseodymium ions in $CaGa_2S_4$ from 3 to 7 at.% leads to a twofold increase in the integrated PL intensity in the range of 470–760 nm.

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