

PHOTOLUMINESCENCE OF $\text{CaGa}_2\text{S}_4:\text{Nd}^{3+}$ COMPOUND

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The investigation results of excitation and photoluminescence spectra (PhL) of CaGa_2S_4 compound activated by neodymium ions (Nd) at room temperature are given. It is seen that the Stokes luminescence connected with electron transitions ${}^2\text{G}_{7/2} \rightarrow {}^4\text{I}_{9/2}$, ${}^2\text{G}_{5/2} \rightarrow {}^4\text{I}_{9/2}$, ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{9/2}$, ${}^4\text{F}_{19/2} \rightarrow {}^4\text{I}_{9/2}$ and ${}^2\text{H}_{9/2} \rightarrow {}^4\text{I}_{9/2}$ of neodymium ions is observed. It is revealed that the PhL intensity increases with Nd concentration increasing.

Keywords: excitation and photoluminescence spectra, Stokes luminescence.

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INTRODUCTION

CaGa_2S_4 compound belongs to the group of triple chalcogenides with general formula of II-III₂-VI₄ (where II are Ba, Sr, Ca, Eu bivalent cations; III₂ are Ga, In, Al trivalent cations; VI₄ 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. 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 [1-6].

The investigation results of CaGa_2S_4 compound photoluminescence activated by rare-earth element (REE) neodymium.

EXPERIMENT TECHNIQUE

CaS compound synthesis is carried out in quartz reactor by interaction of thin-dispersed powder of calcium carbonate (CaCO_3) with flow of hydrogen sulfide (H_2S) and carbon sulfide (CS_2) in atmosphere of (Ar) argon (inert gas) the feed rate of which is 2-2,5l/h. The hydrogen sulfide and carbon sulfides form as a result of dissociation of (NH_4CNS) dehydrated thiocyanate ammonium in gyrator of gas-reagents at temperature 250°C . The synthesis temperature is 720°C - 770°C and it is controlled with the help of chromel-alumel thermo-couple and its duration is 24 hours.

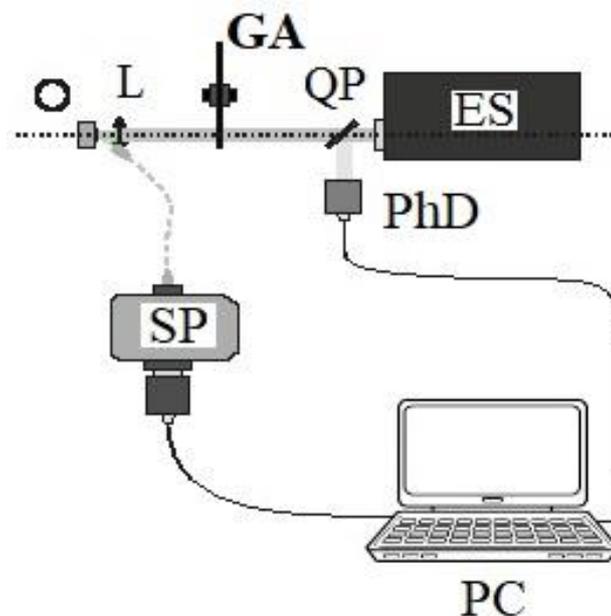
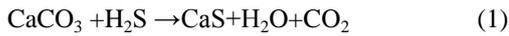
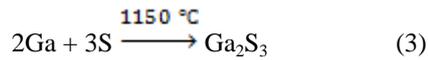


Fig.1. The installation principle circuit for PhL spectrum measurement. O is sample in holder, GA is gradient attenuator, QP is quartz plate, ES is excitation sources, PhD is photodiode measurer of power or impulse energy (Thorlabs inc., Ophir inc.), PC is personal computer.

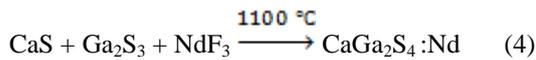
The synthesis takes place by following reactions:



Ga_2S_3 compound is synthesized by the melting of Ga and S in quartz ampoules evacuated up to vacuum $\sim 10^{-4}$ millimeter of mercury by following reaction:



$\text{CaGa}_2\text{S}_4:\text{Nd}$ compound is synthesized by method of solid-phase reaction from CaS, Ga_2S_3 and NdF_3 powder components taken in stoichiometric ratios in quartz ampoules evacuated up to ~ 10 millimeter of mercury by reaction:



The synthesis is carried out at 1400K in one-temperature furnace during 1 hour. The annealing during 4 hours at 1100K is carried out after synthesis. The neodymium ions are introduced into ampoule directly during the synthesis in the form of neodymium fluoride (NdF_3) [7-11]. The precision of ion radiuses of REE (0,80÷1,04) and Ca (0,99) promotes to isomorphous implantation of activator into matrix that causes the luminescence high brightness and line sharpness in luminescence spectra. The presence of cation vacancies or the co-activator penetration (for example fluorine) is the one of the possible ways of charge compensation at substitution of RRE trivalent cation by Ca bivalent cation.

PhL measurements of investigated powder mediums are carried out on installation the principle circuit of which is presented in fig.1. The investigated sample is fixed in holder positioned on three-position linear translator, the displacement scale gradation of which is $10\mu\text{m}$ in any direction.

The continuous HeCd-laser (325 nm) is used as the excitation source in carried experiments at PhL study. The radiation of excitation source is diaphragmed with the aim of use of more its homogeneous part and is focused on sample surface using the spherical lens. The excitation level is estimated taking into consideration the radiation power (or impulse energy) of pumping source and square of excited region. The time-average excitation power is controlled by photodiode measurer. The square of excited region is calculated by laser spot size defined with the help of optic microscope.

The attenuation of exciting radiation is carried out by rotary filter of alternative transmission which allows carrying out the continuous intensity reconstruction in range more than 2 orders. The attenuators with fixed attenuation factor are used jointly with rotary filter in the case of more wide range of excitation level.

The PhL wide bands of chalcogenide semiconductor samples activated by RRE ions are registered with the help of optical fibers by spectrometer equipped by element strip with sequential charge coupling (SCC). For measurement of weak signals the big exposure time is chosen and the averaging by several measurements (usually up to 100) is used for signal/noise parameter improvement.

PhL excitation spectrum is defined as the signal intensity dependence of some PhL spectrum band on exciting radiation wave length. The measurement of PhL excitation spectra is carried out in installation presented in fig.2 in the diagram form. The xenon lamp radiation transmitted through excited monochromator with the aim of isolation from spectrum of its lightening of interested wave length is used as the excitation source. The diminished image of monochromator output slit formed by compound condenser is put on the surface of investigated sample. The power density of exciting radiation is $\sim 10^{-4}$ Wt/cm^2 in dependence on spectral range and widths of monochromator splits. The investigated sample radiation is accumulated with the help of condenser on output split of registering monochromator to output of which the photoelectric multiplier (PhEM) is switched on. The optical signal in PhEM is transformed into electric one which is amplified and quantized by lock-in amplifier and further, the data is sent to computer.

The use of lock-in amplifier instead of usual one for signal amplifying from PhEM allows us to eliminate the limitation on dynamic range of registration system caused by the presence of PhEM dark current. It takes place because of selectivity of lock-in amplifier on signal frequency. The continuous exciting radiation is modulated by shutter with given frequency (usually 80Hz). The signal from shutter is given to output of lock-in amplifier which automatically tunes its spectrum on this frequency. This allows us to decrease the general noise level and avoid the zero drift influence of PhEM caused by dark current. In this case the parasitic background light is automatically removed.

The measurement of PhL excitation spectra is carried out by the way of continuous varying in some interval of exciting radiation wave length (by the means of diffraction lattice angle change of exciting monochromator) at fixed wave length of PhL registered signal and corresponding data reading on this signal intensity from amplifier. The reradiation of investigated sample is focused on split of registered monochromator with the help of condenser. Moreover, the reflected pumping radiation is directed behind the condenser aperture with the aim of influence decrease of scattered radiation. The lamp spectrum taking into consideration the transfer function of exciting monochromator is measured with the help of silicon photodiode with known spectral sensitivity. The ratio of measured PhL excitation spectrum to exciting lamp spectrum corrected with taking into consideration the silicon photodiode sensitivity is taken as required PhL excitation spectrum.

PhL spectrum survey takes place by the means of continuous varying of registered monochromator wave length at constant exciting wave length. The change of registered monochromator wave length is similarly

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carried out to exciting monochromator, i.e. by the means of rotation of monochromator diffraction lattice by the mechanism with step motor.

The program for control of monochromator and lock-in amplifier is written for carrying out of measurements in given installation. The program allows us to measure both PhL spectra and excitation PhL spectra. The dynamic range of the given installation is 3-4 intensity order that is caused by characteristics of monochromators in given installation.

RESULT DISCUSSION.

The maxima at wave length 300nm and 4509nm (fig.3a), 540, 600, 750, 825 nm (fig.3b) are observed in excitation spectra of $\text{CaGa}_2\text{S}_4:\text{Nd}$ compound. At $\lambda = 490$ nm the excitation intensity strongly decreases. PhL spectra taken at room temperature at light excitation

by wave length 325 nm at neodymium different concentrations (1- 5%) are shown in fig.4. 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 ${}^2\text{G}_{7/2} \rightarrow {}^4\text{I}_{9/2}$, ${}^2\text{G}_{5/2} \rightarrow {}^4\text{I}_{9/2}$, ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{9/2}$, ${}^4\text{F}_{19/2} \rightarrow {}^4\text{I}_{9/2}$ and ${}^2\text{H}_{9/2} \rightarrow {}^4\text{I}_{9/2}$ transitions. It is shown that observable PhL 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 PhL 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 non-equivalent luminescence centers in this compound differing on the intensity.

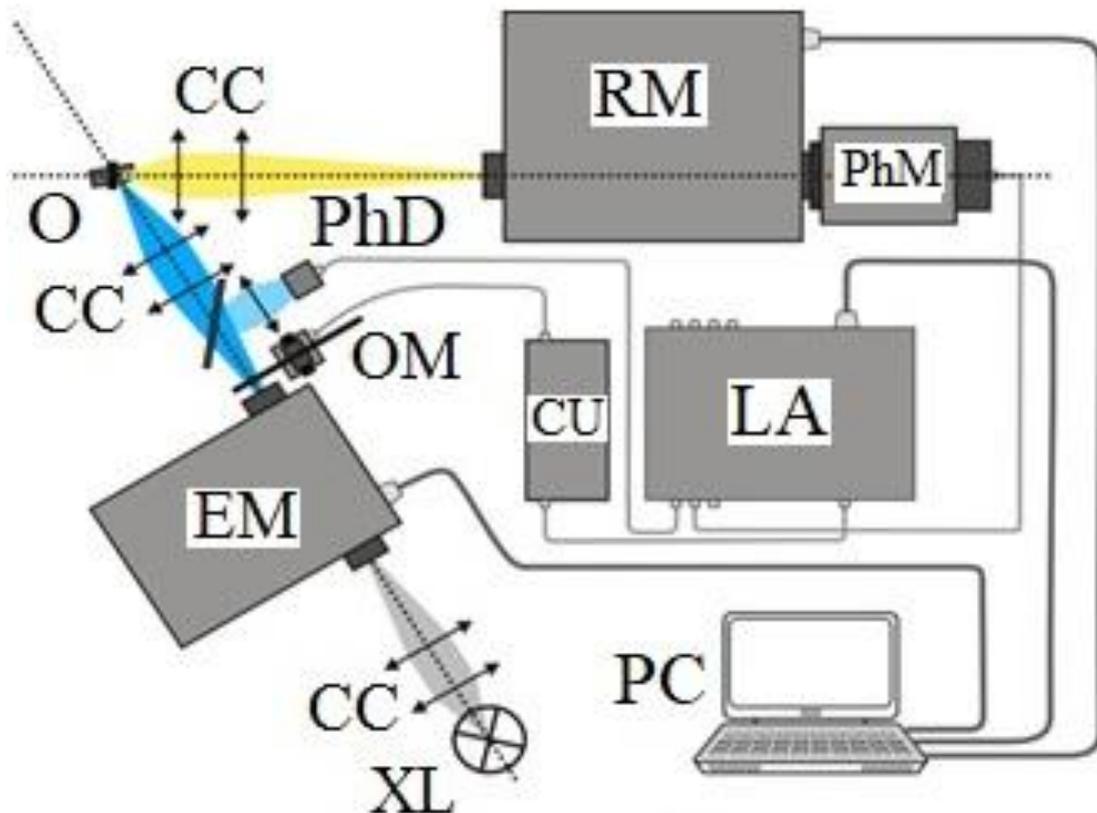
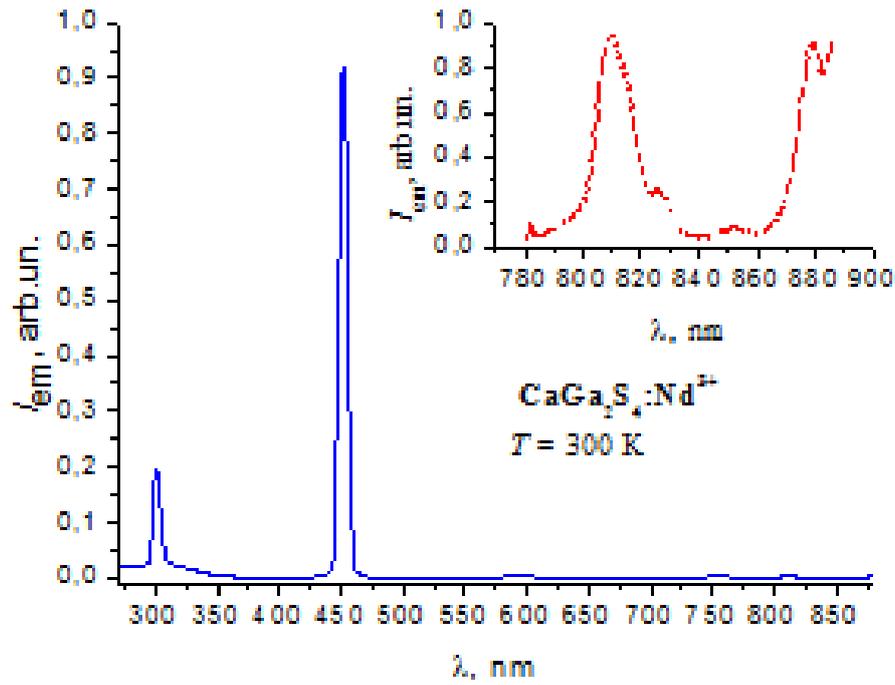
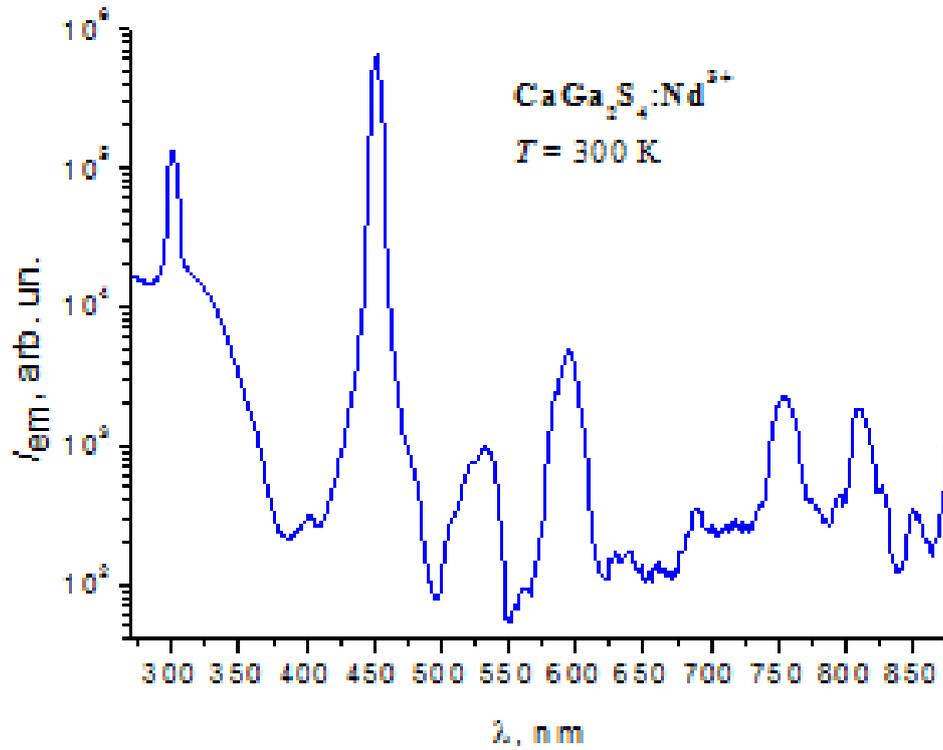


Fig. 2. The installation principal circuit for measurements of PhL excitation spectra. O is sample in holder in open air or cryostat, XL is xenon lamp ДКСШ-120, EM is exciting monochromator МДР-12, RM is registered monochromator МДР-23, CC is composite condenser, CL is convergent spherical lens, OM is optical modulator MC1000 (Thorlabs Inc.), CU is control unit by OM, LA is lock-in amplifier MC 500 (Scitek Instruments), PhD is photodiode measurer of power (Thorlabs PM100), PhM is photomultiplier Hamamatsu, PC is personal computer.



a)



b)

Fig. 3. PL excitation spectra of $\text{CaGa}_2\text{S}_4:\text{Nd}^{3+}$ (5 at.%) compound at room temperature.

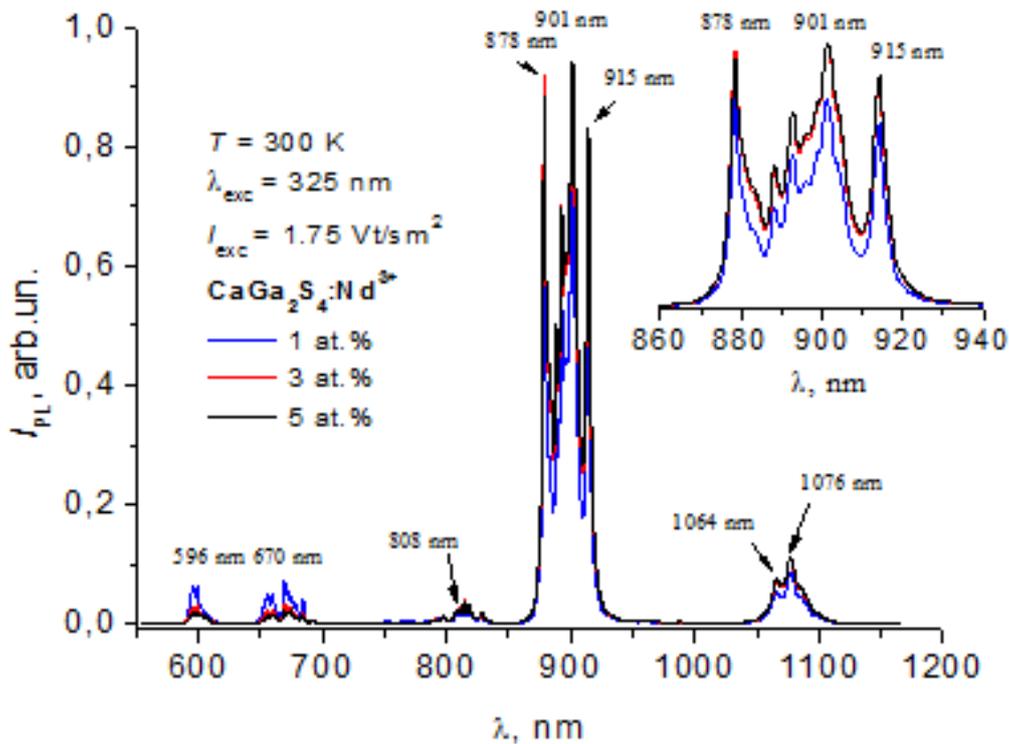


Fig. 4. PhL excitation spectra at 325 nm and 300K.

CONCLUSION

The pumping of impurity rare-earth ion in the investigated $\text{CaGa}_2\text{S}_4:\text{Nd}$ triple compound can take place both through its absorption line and interband transition.

The intracenter radiation of Nd^{3+} corresponding to transitions both from ${}^2\text{G}_{7/2} \rightarrow {}^4\text{I}_{9/2}$, ${}^2\text{G}_{5/2} \rightarrow {}^4\text{I}_{9/2}$, ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{9/2}$, ${}^4\text{F}_{19/2} \rightarrow {}^4\text{I}_{9/2}$ and ${}^2\text{H}_{9/2} \rightarrow {}^4\text{I}_{9/2}$ levels and more high ones is observed at interband excitation.

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