

Optical spectroscopy and local structure of the Nd³⁺ luminescence centres in glasses of the CaO–Ga₂O₃–GeO₂ system

BOHDAN PADLYAK^{1*}, WITOLD RYBA-ROMANOWSKI², RADOSŁAW LISIECKI²

¹Institute of Physical Optics of the Ministry of Education and Science of Ukraine, 23 Dragomanov Str., 79-005, Lviv, Ukraine

²Institute of Low Temperatures and Structure Research, Polish Academy of Sciences, 2 Okólna Str., 50-422 Wrocław, Poland

*Corresponding author: bpadlyak@ifp.lviv.ua

Optical absorption and luminescence spectra as well as luminescence kinetics of the Nd³⁺ centres in glasses with Ca₃Ga₂Ge₃O₁₂:Nd composition, containing 0.2 and 1.0 wt% of the Nd₂O₃ were presented and analysed. The oscillator strengths and phenomenological intensity parameters Ω_t (Ω_2 , Ω_4 , and Ω_6) were obtained using standard Judd–Ofelt theory. Calculated Ω_t parameters, radiative transitions rates, branching ratios and radiative lifetime for Nd³⁺ centres in the glass with Ca₃Ga₂Ge₃O₁₂ composition were analysed and compared with corresponding Nd³⁺ parameters in their crystalline analogue with garnet structure. Experimental lifetimes are compared with those calculated, and quantum efficiency of Nd³⁺ centres from ⁴F_{3/2} emitting level in the glass with Ca₃Ga₂Ge₃O₁₂ composition is estimated. Incorporation peculiarities and local structure of Nd³⁺ luminescence centres in the glass with Ca₃Ga₂Ge₃O₁₂ composition and corresponding Ca₃Ga₂Ge₃O₁₂:Nd³⁺ garnet laser crystals are considered. On the basis of extended X-ray absorption fine structure (EXAFS) spectra (*L*₃-edge) of rare-earth elements analysis it has been shown that Nd³⁺ luminescence centres in the CaO–Ga₂O₃–GeO₂ glass network occupy structural sites with the coordination number to oxygen *N* = 6.

Keywords: germanate glasses, Nd³⁺ centre, optical absorption, luminescence, decay kinetics, extended X-ray absorption fine structure (EXAFS), local structure.

1. Introduction

Glasses and crystals activated with Nd³⁺ ions, especially phosphate glasses [1, 2] and garnet crystals [3–6], are still attractive as an active media for powerful solid-state lasers. That gives rise to intensive spectroscopic investigations of the electron and local structure of luminescence centres in different Nd-doped materials. Traditional laser garnets such as YAG:Nd³⁺ [3] and GSGG:Cr³⁺, Nd³⁺ [7] are characterised by good

spectroscopic and lasing properties, but their synthesis is very expensive and difficult, because these crystals have too high melting temperature (1960 °C and 1850 °C, respectively). The multicationic laser garnets such as $\text{Ca}_3(\text{Nb,Ga})_2\text{Ga}_3\text{O}_{12}:\text{Nd}^{3+}$ [8], $\text{Ca}_3\text{Ga}_2\text{G}_3\text{O}_{12}:\text{Nd}^{3+}$ (CGGG: Nd^{3+}) [9, 10], and $\text{Ca}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}:\text{Nd}^{3+}$ (CaSGG: Nd^{3+}) [11] are characterised by compositionally (or substitutionally) disordered structure and relatively low melting temperatures in the 1450–1460 °C range. Compositional disordering of the $\text{Ca}_3(\text{Nb,Ga})_2\text{Ga}_3\text{O}_{12}$ garnet crystal is related to statistical filling of the octahedral sites by Nb and Ga atoms, what leads to Nd^{3+} optical multisites. Disordering of $\text{Ca}_3\text{Ga}_2\text{G}_3\text{O}_{12}:\text{Nd}^{3+}$ and $\text{Ca}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}:\text{Nd}^{3+}$ crystals is caused by compensation redistribution of Ga^{3+} and Ge^{4+} cations on octahedral and tetrahedral sites of garnet structure at heterovalent $\text{Nd}^{3+} \rightarrow \text{Ca}^{2+}$ substitution. This compensation redistribution leads to the creation of antisite defects of the $\text{Ga}_{(d)}^{3+}$ (Ga^{3+} in tetrahedral (*d*)-sites) and $\text{Ga}_{[a]}^{4+}$ (Ge^{4+} in octahedral [*a*]-sites) types [12, 13] and to the formation of several types of Nd^{3+} centres in dodecahedral {*c*}-sites with different local environments in the second coordination sphere.

The study of optical properties of Nd^{3+} ions in disordered crystals by spectroscopic methods, in particular the resolution and identification of the non-equivalent luminescence centres with different local environments, is essential for a deep understanding of their spectroscopic and laser properties, because laser action is possible when Nd^{3+} ions are located in specific sites [14, 15]. One can notice that Nd^{3+} -doped glasses, garnets and other compositionally disordered crystals are promising materials for solid-state lasers with laser emitting diode (LED) pumping [1, 16–20]. The Nd^{3+} -doped compounds of $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$ system, which can be obtained in both crystalline and glassy states, are perspective materials for LED-pumped lasers. Particularly, in the $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$ system, the crystals with garnet ($\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$) and Ca-gallogermanate ($\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$) structure [21, 22] and corresponding glasses of the same composition can be synthesised [23].

Optical, luminescence and laser properties of the CGGG: Nd^{3+} garnet crystal are described in detail in [9, 10, 24–26]. Assuming a D_2 local symmetry, the Nd^{3+} Stark energy levels in the CGGG crystal are identified, and using the Judd–Ofelt theory, some relevant spectroscopic parameters for laser applications (radiative lifetime, branching ratios and quantum efficiency) from ${}^4F_{3/2}$ emitting level are estimated in [24]. Six non-equivalent Nd^{3+} centres in dodecahedral {*c*}-sites of the CGGG: Nd^{3+} garnet structure are observed in [25] by laser excited site-selective spectroscopy. In [25] the nature and local structure of non-equivalent Nd^{3+} centres in the CGGG: Nd^{3+} crystal in terms of possible charge compensating defects are discussed, and formation of $\text{Nd}^{3+}\text{-Nd}^{3+}$ pairs is suggested. Optical absorption, luminescence characteristics and stimulated emission parameters for ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ and ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$ channels of Nd^{3+} centres in $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ and $\text{Sr}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ compositionally disordered crystals are investigated and analysed in [27].

At present, time high quality Nd-doped glasses with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ garnet composition were obtained according to [23]. Optical absorption and luminescence

spectra as well as luminescence kinetics of Nd^{3+} centres in glasses with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ composition were firstly presented in [28]. It has been shown in [28], by electron paramagnetic resonance (EPR) and optical spectroscopy, that Nd is incorporated into the $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$ glass network exclusively as Nd^{3+} ions ($4f^3$ – electron configuration, $^4I_{9/2}$ – free ion ground state), and all the observed transitions of Nd^{3+} centres in optical spectra were identified. In this paper, the results of optical spectroscopy of Nd^{3+} luminescence centres in the glass with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ composition are summarised and analysed. Optical absorption and emission spectra, luminescence kinetics and basic parameters of Nd^{3+} centres in the glass with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ composition are discussed and compared with corresponding data for garnet crystal of the same composition. Incorporation peculiarities and local structure of Nd^{3+} luminescence centres in the glass and crystal with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ composition are considered.

2. Experimental details

2.1. Characteristics of the investigated samples

The Nd-doped glasses of high chemical purity and optical quality with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ (or $3\text{CaO-Ga}_2\text{O}_3\text{-3GeO}_2$) composition were obtained in corundum crucibles by high-temperature synthesis according to [23]. The Nd impurity was added to the glass composition as Nd_2O_3 oxide in amounts of 0.2 and 1.0 wt%. The colour of obtained Nd-doped glass samples varies depending on the Nd content from almost uncoloured (Nd_2O_3 content – 0.2 wt%) to lightly blue (Nd_2O_3 content – 1.0 wt%). Chemical composition of obtained samples was controlled by X-ray microanalysis technique using a “Camebax” apparatus. Paramagnetic impurities were controlled by EPR technique. For optical measurements samples were polished to approximate size of $6 \times 3 \times 2 \text{ mm}^3$. For EPR spectroscopy glass samples were cut to approximate size of $4 \times 2 \times 2 \text{ mm}^3$.

By X-ray scattering, molecular dynamics simulations and extended X-ray absorption fine structure (EXAFS) spectroscopy, it has been shown that mixed tetrahedral $(\text{Ge}/\text{Ga})\text{O}_4$ and octahedral $(\text{Ge}/\text{Ga})\text{O}_6$ groups are basic structural units in glasses of the $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$ system [29, 30]. The synthesised Nd-doped glasses with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ composition show a typical glassy-like X-ray structure factor, which is quite similar to the structure factor of the undoped glass of the same composition [29]. Structural investigations of undoped [30] and rare-earth doped [31] glasses with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ composition by EXAFS technique show that incorporation of Nd^{3+} and other rare-earth ions changes the local structure only around Ga atoms (Ga short-range order), whereas the Ge short-range order is almost independent of rare-earth doping and it is similar to the short-range order of undoped glasses of the same composition. Results of direct EXAFS investigation of the local environment of rare-earth impurity ions in the glass with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ composition were presented and analysed in [32].

2.2. Experimental methods and equipment

Optical absorption spectra were registered at room and liquid nitrogen temperatures on a Carl Zeiss Jena (model Specord M-40) spectrophotometer. Photoluminescence spectra were measured in the 4.2–300 K temperature range using equipment built in the Institute of Low Temperatures and Structure Research of the Polish Academy of Sciences (Wrocław, Poland). Luminescence spectra were excited by an Ar ion laser operating at $\lambda = 514.5$ nm. Luminescence spectra were recorded at room temperature with a Dongwoo (model DM 711) scanning monochromator having 750 mm focal length equipped with an InGaAs detector. Low temperature emission spectra were dispersed with a double grating monochromator (focal length – 1 m) and detected by a photomultiplier with S-1 spectral response.

Luminescence decay curves were recorded with a Tektronix (model TDS 3052) digital oscilloscope. Excitation was provided by a continuum surelite I optical parametric oscillator (OPO) pumped by a third harmonic of an YAG:Nd³⁺ laser ($\lambda = 355$ nm). For low temperature measurements, samples were mounted in an Oxford (model CF 2104) continuous flow liquid helium cryostat equipped with a temperature controller.

3. Results and discussion

3.1. Optical spectra of Nd³⁺ centres

The Nd impurity in oxide crystals and glasses appears to be Nd³⁺ ($4f^3$, $^4I_{9/2}$) and Nd²⁺ ($4f^4$, 5I_4) ions with characteristic EPR and optical spectra. In the Nd-doped glass with Ca₃Ga₂Ge₃O₁₂ composition at liquid helium temperatures only Nd³⁺

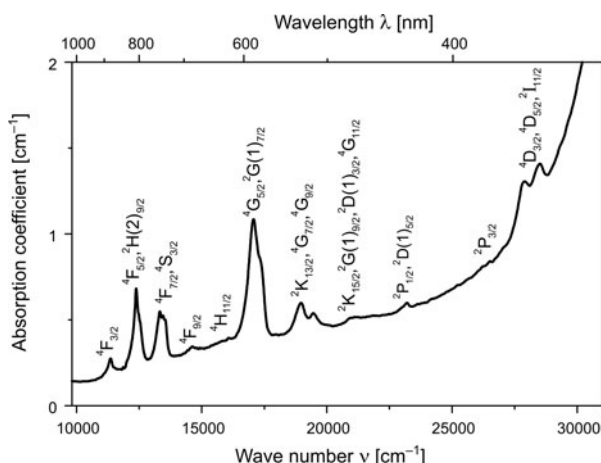


Fig. 1. Optical absorption spectrum of Nd³⁺ centres in the glass with Ca₃Ga₂Ge₃O₁₂:Nd composition containing 0.2 wt% of Nd₂O₃, recorded at $T = 293$ K.

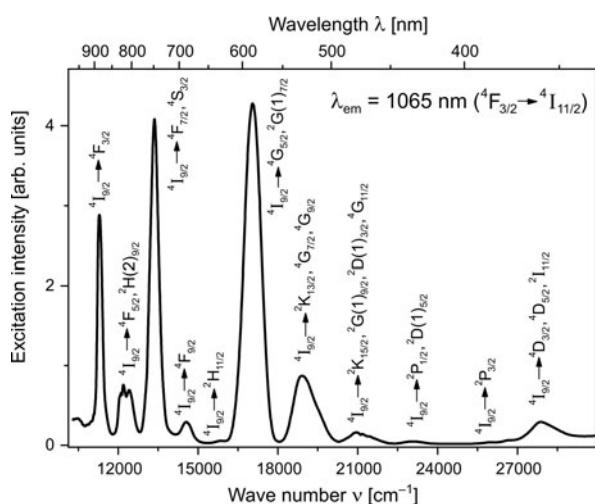


Fig. 2. Luminescence excitation spectrum of Nd^{3+} centres in the glass with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}:\text{Nd}$ composition containing 1.0 wt% of Nd_2O_3 , recorded at $T = 293$ K.

EPR spectrum was observed. This result shows that Nd impurity is incorporated into the $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ glass network as Nd^{3+} ions.

The undoped glasses of the $\text{CaO}-\text{Ga}_2\text{O}_3-\text{GeO}_2$ system are transparent in the UV region up to 280–300 nm and are characterised by high transparency in the IR spectral range [23]. Optical absorption spectrum of the Nd-doped glass with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ composition in 340–1000 nm ($10000-30000\text{ cm}^{-1}$) spectral range at room temperature consists of several absorption bands with weakly resolved structure and belongs to Nd^{3+} ions (Fig. 1). The linewidth and resolution of Nd^{3+} absorption bands practically were not changed at lowering temperature up to liquid nitrogen, which is the evidence of the inhomogeneous broadening, related to disordering of glass structure. As a result, some observed complex and weakly-resolved Nd^{3+} bands can be assigned to groups of absorption transitions (Fig. 1). In accordance with Nd^{3+} energy level diagram and referenced data [33, 34] all observed absorption bands were assigned to appropriate electronic $f-f$ transitions from $^4I_{9/2}$ ground state to excited states, which are identified in Fig. 1.

In the luminescence excitation spectrum of Nd^{3+} ions, 11 weakly-resolved and unresolved bands (Fig. 2) were observed at room temperature, which shows good correlation with optical absorption transitions (Fig. 1). One can notice that the intensity of $^4I_{9/2} \rightarrow ^2P_{3/2}$ and $^4I_{9/2} \rightarrow ^2H_{11/2}$ transitions of Nd^{3+} centres weakly appears in the excitation (Fig. 2) and optical absorption (Fig. 1) spectra of the glass samples, containing 0.2 and 1.0 wt% of Nd_2O_3 .

The Nd^{3+} emission spectrum, recorded at room temperature in the 800–1500 nm spectral range under excitation with Ar laser in the absorption band which corresponds to $^4I_{9/2} \rightarrow (^2K_{13/2}, ^4G_{7/2}, ^4G_{9/2})$ transitions is presented in Fig. 3a. The observed

luminescence spectrum of Nd^{3+} ions consists of three characteristic bands which correspond to following transitions: ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ ($\lambda_{\text{max}} \cong 910$ nm), ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ ($\lambda_{\text{max}} \cong 1065$ nm), and ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$ ($\lambda_{\text{max}} \cong 1339$ nm) (Fig. 3a). No better resolution of ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ and ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$ emission bands was observed at liquid helium temperatures (Fig. 3b), which is the evidence of inhomogeneous broadening of spectral lines, caused by disordering of glass structure.

The observed optical absorption and luminescence spectra of Nd^{3+} ions in glasses of the $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$ system are almost independent of basic glass composition and temperature in the 4.2–300 K range and are quite similar to optical spectra in other

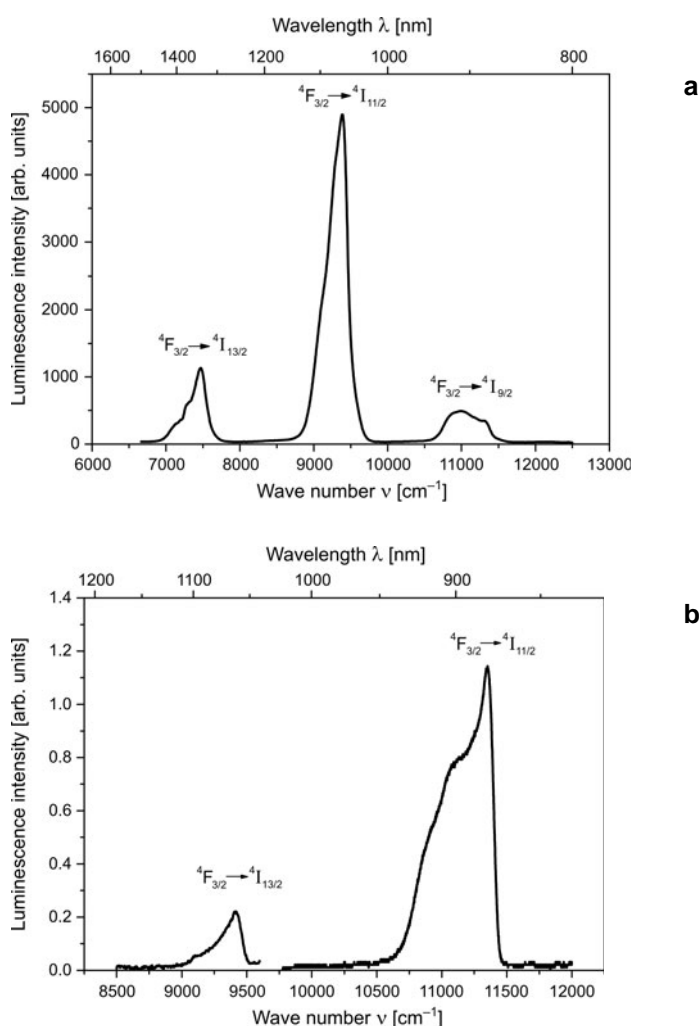


Fig. 3. Luminescence spectra of Nd^{3+} centres in the glass with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}:\text{Nd}$ composition containing 1.0 wt% of Nd_2O_3 under excitation with Ar laser ($\lambda_{\text{exc}} = 514.5$ nm), recorded at $T = 293$ K (a) and $T = 10$ K (b).

Nd^{3+} -doped oxide glasses [35–37] and compositionally-disordered Ca-gallogermanate ($\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$) crystals [27].

3.2. Luminescence kinetics of Nd^{3+} centres

Luminescence decay curves for ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition ($\lambda_{\text{max}} \cong 1065 \text{ nm}$) of Nd^{3+} centres in the glass with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}:\text{Nd}$ composition and different Nd_2O_3 content are presented in Fig. 4. The observed decay curves were satisfactorily described by one-exponential decay with lifetimes $\tau = 342 \mu\text{s}$ and $\tau = 290 \mu\text{s}$ for samples containing 0.2 and 1.0 wt% of Nd_2O_3 , respectively (Figs. 4a and 4b). Lowering of the lifetime value in the sample with 1.0 wt% of Nd_2O_3 in comparison with the lifetime in the sample with 0.2 wt% of Nd_2O_3 is related to the saturation effect which appears at high concentration of luminescence centres. In the $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}:\text{Nd}$ glass containing

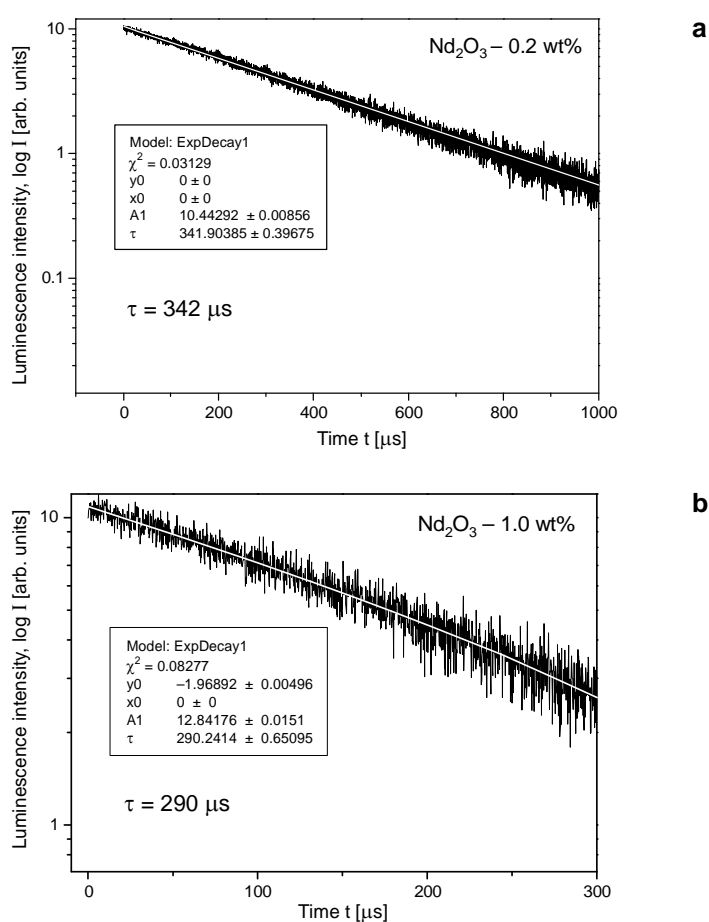


Fig. 4. Luminescence decay curves for Nd^{3+} centres (${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition, $\lambda_{\text{max}} = 1065 \text{ nm}$), recorded at $T = 293 \text{ K}$ in the glass with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}:\text{Nd}$ composition containing 0.2 wt% (a) and 1.0 wt% (b) of Nd_2O_3 . Black lines with noises – experimental, white solid lines – results of one-exponential fit.

0.2 wt% of Nd_2O_3 small increasing of the Nd^{3+} luminescence lifetime was observed in the 4.2–300 K range, whereas in the glass doped with 1.0 wt% of Nd_2O_3 , the Nd^{3+} lifetime practically was not changed with temperature [28].

The obtained lifetime values for Nd^{3+} centres and their temperature dependences show good correlation with corresponding literature data for glasses with other compositions [35, 36, 38, 39]. In silicate glasses, the Nd^{3+} lifetime in the ${}^4F_{3/2}$ level $\tau = 380 \mu\text{s}$ at $T = 300 \text{ K}$ [39]. In silicate-phosphate glasses with $56\text{CaO}-35\text{SiO}_2-9\text{P}_2\text{O}_5$ composition, the Nd^{3+} lifetime $\tau = 330 \mu\text{s}$ and is independent of temperature in the 10–300 K range for samples containing $\approx 0.07 \text{ wt}\%$ of Nd_2O_3 , whereas for samples containing 1–4 wt% of Nd_2O_3 $\tau \approx 295 \mu\text{s}$ at $T = 10 \text{ K}$ and $\tau \approx 245 \mu\text{s}$ at $T = 300 \text{ K}$ [38]. In the $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}:\text{Nd}^{3+}$ laser garnet (crystalline analogy of the investigated glass) containing $\approx 0.8 \text{ at}\%$ of Nd_2O_3 , the Nd^{3+} centres are characterised by approximately single-exponential luminescence decay with the lifetime $\tau = (210 \pm 10) \mu\text{s}$ at 4.2 and 77 K [9, 24]. Six non-equivalent Nd^{3+} centres, observed in dodecahedral $\{c\}$ -sites of the $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ garnet structure with different local environments in the second coordination sphere [25], were not resolved in the luminescence kinetics. The obtained lifetime value $\tau = (210 \pm 10) \mu\text{s}$ in [9] is assigned to Nd^{3+} centres with most probable local environment in the $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ crystal structure. In the $\text{Ca}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}:\text{Nd}^{3+}$ garnet crystal with the composition closely similar to $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}:\text{Nd}^{3+}$ garnet and investigated glass, the Nd^{3+} luminescence ($F_{3/2} \rightarrow {}^4I_{11/2}$ transition, $\lambda_{\text{max}} = 1060 \text{ nm}$) in the 10–298 K temperature range is also characterised by single exponential decay with $\tau = (254 \pm 2) \mu\text{s}$ which corresponds to one type of Nd^{3+} centres, despite the presence of several types of centres with different local environments [11].

The lifetimes of Nd^{3+} centres in $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ [9] and $\text{Ca}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}$ [11] crystals and glasses with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ composition [28] are independent or weakly-dependent on temperature and quantum efficiency of luminescence from ${}^4F_{3/2}$ level which is close to 100%. These results can be understood for $\text{Ca}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}:\text{Nd}^{3+}$ crystal, because the energy between emitting ${}^4F_{3/2}$ and the lowest excited ${}^4I_{11/2}$ levels equals $\approx 5300 \text{ cm}^{-1}$, which corresponds to six quanta with the highest phonon frequency (804 cm^{-1}), observed in this crystal. A similar situation was observed in the crystal and glass with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}:\text{Nd}^{3+}$ composition. Presented results show that the multiphonon relaxation from ${}^4F_{3/2}$ level in compounds of $\text{CaO}-\text{Ga}_2\text{O}_3-\text{GeO}_2$ and $\text{CaO}-\text{Sc}_2\text{O}_3-\text{GeO}_2$ systems is negligible.

3.3. The Judd–Ofelt analysis and spectroscopic parameters of Nd^{3+} centres

Transition energies and relative intensities of Nd^{3+} absorption bands in the glass with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ composition were analysed on the basis of Judd–Ofelt theory [40, 41]. Using a standard program for Judd–Ofelt calculations, oscillator strengths (f_{theor}) and intensity parameters ($\Omega_2, \Omega_4, \Omega_6$) for observed transitions of Nd^{3+} centres in the $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ glass were obtained (Tab. 1). By comparison, Tab. 1 also presents oscillator strengths (f_{exp}) calculated from average energies of the maxima (\bar{E}) of the experimental absorption bands and Judd–Ofelt intensity parameters ($\Omega_2, \Omega_4, \Omega_6$)

Table 1. Results of the Judd–Ofelt analysis for Nd^{3+} centres in the glass with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}:\text{Nd}$ garnet composition.

Absorption transitions $^4I_{9/2} \rightarrow$	Energy [cm^{-1}]	Oscillator strength f_{exp}	Oscillator strength f_{theor}	Difference
$^4F_{3/2}$	11284	$8.20 \cdot 10^{-7}$	$9.32 \cdot 10^{-7}$	$1.12 \cdot 10^{-7}$
$^4F_{5/2} + ^2H(2)_{9/2}$	12344	$4.97 \cdot 10^{-6}$	$4.70 \cdot 10^{-6}$	$2.75 \cdot 10^{-7}$
$^4F_{7/2} + ^4S_{3/2}$	13387	$4.06 \cdot 10^{-6}$	$4.06 \cdot 10^{-6}$	0.00
$^4F_{9/2}$	14625	$4.06 \cdot 10^{-7}$	$3.09 \cdot 10^{-7}$	$0.97 \cdot 10^{-7}$
$^4G_{5/2} + ^2G(1)_{7/2}$	17164	$1.58 \cdot 10^{-5}$	$1.58 \cdot 10^{-5}$	0.00
$^2K_{13/2} + ^4G_{7/2} + ^4G_{9/2}$	19252	$4.22 \cdot 10^{-6}$	$4.47 \cdot 10^{-6}$	$2.47 \cdot 10^{-7}$
$^2K_{15/2} + ^2G(1)_{9/2} + ^2D(1)_{3/2} + ^4G_{11/2}$	21380	$8.32 \cdot 10^{-7}$	$9.62 \cdot 10^{-7}$	$1.31 \cdot 10^{-7}$
$^2P_{1/2} + ^2D(1)_{5/2}$	23290	$6.35 \cdot 10^{-7}$	$5.93 \cdot 10^{-7}$	$0.42 \cdot 10^{-7}$
$^2P_{3/2}$	26203	$2.76 \cdot 10^{-7}$	$2.16 \cdot 10^{-7}$	$0.60 \cdot 10^{-7}$
$^4D_{3/2} + ^4D_{5/2} + ^2I_{11/2}$	28048	$5.62 \cdot 10^{-6}$	$5.62 \cdot 10^{-6}$	0.00
Judd–Ofelt intensity parameters Ω [cm^2]	$\Omega_2 = 2.29 \cdot 10^{-20}$, $\Omega_4 = 2.98 \cdot 10^{-20}$, $\Omega_6 = 1.85 \cdot 10^{-20}$ ($\Omega_2 = 0.98 \cdot 10^{-20}$, $\Omega_4 = 3.96 \cdot 10^{-20}$, $\Omega_6 = 5.94 \cdot 10^{-20}$)*			

*For comparison, in parentheses, are given the calculated Judd–Ofelt intensity parameters for Nd^{3+} centres in the $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ laser garnet crystal [24].

Table 2. Calculated rates of the spontaneous electro-dipole transitions W_r , branching ratios β , and radiative lifetime τ_{rad} for emission from $^4F_{3/2}$ level of the Nd^{3+} centres in the glass with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ garnet composition.

Emission transitions $^4F_{3/2} \rightarrow$	Transitions energy [cm^{-1}]	W_r [s^{-1}]	β
$^4I_{9/2}$	11284	721.16 (1904.88)	0.3307 (0.3937)
$^4I_{11/2}$	9170	1242.62 (2400.71)	0.5699 (0.4962)
$^4I_{13/2}$	7186	209.46 (508.10)	0.0961 (0.1050)
$^4I_{15/2}$	5136	7.25 (24.18)	0.0033 (0.0050)
		$\Sigma W_r = 2180.49 \text{ s}^{-1}$	
		$\tau_{\text{rad}}(^4F_{3/2}) = 459 \text{ } \mu\text{s}$	
		$(\tau_{\text{rad}}(^4F_{3/2})) = 206.7 \text{ } \mu\text{s}$	

Note: For comparison, in parentheses are given the calculated rates of the spontaneous electro-dipole transitions W_r , branching ratios β , and radiative lifetime τ_{rad} for emission from $^4F_{3/2}$ level of the Nd^{3+} centres in the $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ laser garnet crystal [24].

for Nd^{3+} centres in the $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ laser garnet crystal [24]. Differences between theoretical (f_{theor}) and experimental (f_{exp}) oscillator strengths for all observed Nd^{3+} absorption bands in the glass with garnet composition are negligible (Tab. 1), which shows good correlation of the experimental data with Judd–Ofelt theory. A significant difference between intensity parameters, especially Ω_2 and Ω_6 , in the glass and crystal with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ composition (Tab. 1) shows an essentially different distortion of the local environment for Nd^{3+} centres in the glass network and crystal lattice.

Using the obtained Ω_2 , Ω_4 , and Ω_6 parameters, the radiative transition rates (W_r), branching ratios (β) for ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$, ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$, ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$, and ${}^4F_{3/2} \rightarrow {}^4I_{15/2}$ electro-dipole transitions and radiative lifetime (τ_{rad}) for ${}^4F_{3/2}$ metastable level of Nd^{3+} centres in the glass with garnet composition were calculated from standard relations, given in [24]. The obtained spectroscopic parameters of Nd^{3+} centres in the glass with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ composition, which are of relevance for laser applications (W_r , β , and τ_{rad}), are presented in Tab. 2, where the corresponding parameters of the $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}:\text{Nd}^{3+}$ laser garnet crystal are also shown. The calculated rates W_r for Nd^{3+} spontaneous electro-dipole transitions ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ and ${}^4F_{3/2} \rightarrow {}^4I_{15/2}$ in $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ crystal are approximately 3 times larger, and for ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$, ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$ and ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transitions 2 times larger than those in the glass of the same composition (Tab. 2). Branching ratios β for all emission transitions in the crystal are larger than those in the glass. The ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ channel in the glass with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ composition is characterised by the largest branching ratio and can be used for laser generation. The calculated radiative lifetime τ_{rad} of Nd^{3+} centres in the ${}^4F_{3/2}$ metastable level in the glass with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ composition is more than 2 times larger than the corresponding lifetime in the garnet crystal of the same composition. Quantum efficiency of the spontaneous emission from ${}^4F_{3/2}$ level of Nd^{3+} centres is $\eta \cong 75\%$ in the glass with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}:\text{Nd}$ (Nd_2O_3 content – 0.2 wt%) composition. The calculated η value of Nd^{3+} centres in glass is lower than that in $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}:\text{Nd}^{3+}$ garnet crystal ($\eta \cong 97\%$) [24], but essentially higher than that in fluoroborophosphate glasses ($\eta = 59\text{--}65\%$) [42] and close to Nd^{3+} quantum efficiency in borate ($\eta = 72\text{--}78\%$) and phosphate ($\eta \cong 80\%$) laser glasses [2]. Basing on this analysis, we can conclude that the glass with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}:\text{Nd}^{3+}$ composition is a perspective material for lasers (${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ channel, $\lambda_{\text{max}} \cong 1065$ nm) and in future, from a technological point of view, it will be able to compete with laser phosphate glasses and with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}:\text{Nd}^{3+}$ laser garnet crystal.

3.4. Local structure of the Nd^{3+} centres in the $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ glass network

Presented results, concerning optical spectroscopy and luminescence kinetics analysis, show that in the glass with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ composition exists only one type of Nd^{3+} centres with local environment, distorted by statistically-distributed Ga^{3+} and Ge^{4+} cations in the second coordination sphere, which leads to formation of the ensemble of luminescence centres with distributed spectroscopic parameters. On the basis of published data [9, 11, 24, 25] for Nd^{3+} ions in $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ and other

garnet crystals [28] it has been assumed that Nd^{3+} centres in the glass with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ composition are localised in the sites similar to the dodecahedral sites of the garnet structure with a coordination number $N = 8$.

Due to a detailed analysis of the Eu, Ho, and Er (L_3 -edge) EXAFS spectra, it has been shown that the local structure of these elements in the $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ glass is characterised by $N = 6$ [32], in contrast to the corresponding garnet crystal. In [32] the Nd^{3+} local structure has not been investigated directly by EXAFS method, but in [31] it has been shown that the incorporation of rare-earth (Ce, Nd, Eu, Ho, Er) impurities leads to similar modification of local structure around Ga cations in the glass network. On the basis of results, presented in [31, 32], we can conclude that the local environment of Eu^{3+} , Ho^{3+} , Er^{3+} , and Nd^{3+} luminescence centres in the $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ glass network is the same, and that the first coordination sphere around rare-earth impurity ions consists of six O^{2-} anions. This result shows good agreement with results obtained for Er^{3+} ($N = 6-7$) [43] and Eu^{3+} ($N = 6$) [44] ions in some oxide glasses.

Thus, the local structure of Nd^{3+} and of other rare-earth luminescence centres is essentially different in the glass and crystal of the same composition, because in the garnet lattice, the rare-earth ions generally occupy dodecahedral $\{c\}$ -sites with $N = 8$. Lowering of the coordination number to $N = 6$ for rare-earth ions in the glass, in comparison with their crystalline analogy, can be related to a large number of oxygen vacancies in the glass network. The EXAFS analysis [32] reveals only one type of rare-earth ions sites in the glass network with broad distribution of the interatomic distances in the first coordination sphere. These results show good agreement with optical spectroscopy and luminescence kinetics of the Nd^{3+} centres in the glass with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ composition.

4. Conclusions

On the basis of the analysis of presented results, we can conclude the following:

1. The neodymium impurity is incorporated into the $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ glass network as Nd^{3+} ($4f^3$, $^4I_{9/2}$) ions, exclusively, because the characteristic optical spectra of the Nd^{2+} ($4f^4$, 4I_5) ions were not registered in all investigated samples.

2. Optical spectra of the Nd^{3+} ions in the glasses with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ composition are quite similar to Nd^{3+} optical spectra, observed in other oxide glasses and compositionally-disordered crystals, and are characterised by inhomogeneous broadening of spectral lines. All observed transitions (UV, visible, and IR) of the Nd^{3+} centres in optical absorption, emission and luminescence excitation spectra are identified. Luminescence kinetics of the Nd^{3+} centres for $^4F_{3/2} \rightarrow ^4I_{11/2}$ transition is satisfactorily described by exponential decay with the lifetimes 342 and 290 μs at $T = 293$ K for samples containing 0.2 and 1.0 wt% of Nd_2O_3 , respectively.

3. The Nd^{3+} optical spectra were analysed and described in the framework of Judd–Ofelt theory. Oscillator strengths, Judd–Ofelt intensity parameters (Ω_2 , Ω_4 , Ω_6),

radiative transition rates, branching ratios, and radiative lifetime for Nd^{3+} centres in the glass with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ composition were calculated.

4. Calculated spectroscopic parameters were compared with corresponding data, obtained for $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}:\text{Nd}^{3+}$ laser garnet crystal. It has been shown that the glass with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}:\text{Nd}^{3+}$ composition is a perspective material for lasers, operating in the infrared spectral range ($F_{3/2} \rightarrow {}^4I_{11/2}$ channel, $\lambda_{\text{max}} = 1065$ nm), in particular for LED-pumped lasers.

5. On the basis of presented optical spectroscopy and referenced EXAFS data analysis, it has been shown that the local structure of Nd^{3+} luminescence centres in the glass with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ composition is characterised by the coordination number $N = 6$, at variance with the corresponding garnet crystal, where $N = 8$ for all rare-earth luminescence centres.

Acknowledgements – The authors would like to thank Petro Buchynskii from L'viv Scientific Industrial Amalgamation “MikroTech Karat” for the synthesis of the glass samples. The presentation of this work in the NATO Advanced Research 8th Workshop *Porous Glasses – Special Glasses* is supported in the framework of the NATO Science for Peace and Security Programme.

References

- [1] MAK A.A., SOMS L.N., FROMZEL V.A., YASHIN V.E., *Lasers on the Base of Neodymium Glass*, Nauka, Moskva 1990 (in Russian).
- [2] BROWN D.C., *High-Peak-Power Nd:Glass Laser Systems*, Springer-Verlag, Berlin, Heidelberg, New York 1981.
- [3] GEUSIC J., MARCOS H.M., VAN UITERT L.G., *Laser oscillations in nd-doped yttrium aluminum, yttrium gallium and gadolinium garnets*, Applied Physics Letters **4**(10), 1964, pp. 182–4.
- [4] KAMINSKII A.A., OSIKO V.V., SARKISOV S.E., TIMOSHECHKIN M.I., ZHARIKOV E.V., BOHM J., REICHE P., SHULTZE D., *Growth, spectroscopic investigations, and some new stimulated emission data of $\text{Gd}_3\text{Ga}_5\text{O}_{12}:\text{Nd}^{3+}$ single crystals*, Physica Status Solidi A **49**(1), 1978, pp. 305–11.
- [5] STRUVE B., HUBER G., LAPTEV V.V., SHCHERBAKOV I.A., ZHARIKOV E.V., *Tunable room-temperature cw laser action in $\text{Cr}^{3+}:\text{GdScGa}$ -garnet*, Applied Physics B: Lasers and Optics **30**(3), 1983, pp. 117–20.
- [6] STRUVE B., HUBER G., *Laser performance of $\text{Cr}^{3+}:\text{Gd}(\text{Sc}, \text{Ga})$ garnet*, Journal of Applied Physics **57**(1), 1985, pp. 45–8.
- [7] ZHARIKOV E.V., IL'ICHEV N.N., LAPTEV V.V., MALYUTIN A.A., OSTROUMOV V.G., PASHININ P.P., SHCHERBAKOV I.A., *Sensitization of neodymium ion luminescence by chromium ions in a $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ crystal*, Soviet Journal of Quantum Electronics **12**(3), 1982, pp. 338–41; (original: Kvantovaya Elektronika, Moskva **9**(3), 1982, pp. 568–73).
- [8] CALDIÑO U.G., JAQUE F., BALDA R., FERNÁNDEZ J., KAMINSKII A.A., *Nd^{3+} optical multisites in the $\text{Ca}_3(\text{Nb}, \text{Ga})_2\text{Ga}_3\text{O}_{12}$ laser garnet crystal*, Optical Materials **4**(6), 1995, pp. 713–6.
- [9] ES'KOV N.A., OSIKO V.V., SOBOL' A.A., TIMOSHECHKIN M.I., BUTAEVA T.I., CHAN NGOK, KAMINSKII A.A., *A new laser garnet $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}:\text{Nd}^{3+}$* , Inorganic Materials **14**(12), 1978, pp. 1764–5; (original: Izvestiya Akademii Nauk SSSR, Neorganicheskie Materialy **14**(12), 1978, pp. 2254–5).
- [10] CALDIÑO U., BAUSÁ L.E., GARCÍA SOLÉ J., JAQUE F., KAMINSKII A.A., BUTASHIN A.V., MILL B.V., *Site-selective spectroscopy of Nd^{3+} in the $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ laser crystal*, Journal de Physique IV **4**(C4), 1994, pp. 389–92.

- [11] CAVALLI E., ZANNONI E., BELLETTI A., CAROZZO V., TONCELLI A., TONELLI M., BETTINELLI M., *Spectroscopic analysis and laser parameters of Nd³⁺ in Ca₃Sc₂Ge₃O₁₂ garnet crystals*, Applied Physics B: Lasers and Optics **68**(4), 1999, pp. 677–81.
- [12] PADLYAK B.V., NOSENKO A.E., *Characteristics of isomorphism of manganese in Ca₃Ga₂Ge₃O₁₂:Mn crystals*, Soviet Physics Solid State **30**(6), 1988, pp. 1027–30; (original: Fizika Tverdogo Tela **30**(6), 1988, pp. 1788–92).
- [13] PADLYAK B.V., NOSENKO A.E., MAKSIMENKO V.M., KRAVCHISHIN V.V., *Electron spin resonance spectroscopy of Cr⁵⁺ ions in Ca₃Ga₂Ge₃O₁₂:Cr single crystals*, Physics of the Solid State **35**(9), 1993, pp. 1185–90; (original: Fizika Tverdogo Tela **35**(9), 1993, pp. 2392–401).
- [14] GUYOT Y., BAUSÁ L.E., CAMARILLO E., GARCÍA SOLÉ J., VERGARA I., MONTEIL A., MONCORGÉ R., *Infrared fluorescence spectra of Nd³⁺ sites in gadolinium gallium garnet: Nd and gadolinium gallium garnet: Nd, Cr*, Journal of Applied Physics **72**(12), 1992, pp. 5876–80.
- [15] TOCHO J.O., JAQUE F., GARCÍA SOLÉ J., CAMARILLO E., CUSSÓ F., MUÑOZ SANTIUSTE J.E., *Nd³⁺ active sites in Nd:MgO:LiNbO₃ lasers*, Applied Physics Letters **60**(26), 1992, pp. 3206–8.
- [16] SINGH S., SMITH R.G., VAN UITERT L.G., *Stimulated emission cross section and fluorescent quantum efficiency of Nd³⁺ in yttrium aluminium garnet at room temperature*, Physical Review B: Solid State **10**(6), 1974, pp. 2566–72.
- [17] SARDAR D.K., VIZCARRA S., ISLAM M.A., ALLIK T.H., SHARP E.J., PINTO A.A., *Characterization of spectroscopic properties of Nd³⁺:CaZn₂Y₂Ge₃O₁₂ (CAZGAR)*, Journal of Luminescence **60–61**, 1994, pp. 97–100.
- [18] SARDAR D.K., VIZCARRA S., ISLAM M.A., ALLIK T.H., SHARP E.J., PINTO A.A., *Spectroscopic analysis and the effects of color centers on the laser performance of Nd³⁺:CaZn₂Y₂Ge₃O₁₂*, Optical Materials **3**(4), 1994, pp. 257–63.
- [19] SARDAR D.K., STUBBLEFIELD S.C., *Characterization of Stark components and peak emission cross sections of intermanifold and inter-Stark transitions of Nd³⁺ in Ba_{0.25}Mg_{2.75}Y₂Ge₃O₁₂*, Journal of Applied Physics **80**(9), 1996, pp. 5275–7.
- [20] RYBA-ROMANOWSKI W., *Disordered Nd-doped crystals for diode pumping*, Acta Physica Polonica A **84**(5), 1993, pp. 945–52.
- [21] DAMEN J.P.M., PISTORIUS J.A., ROBERTSON J.M., *Calcium gallium germanium garnet as a substrate for magnetic bubble application*, Materials Research Bulletin **12**(1), 1977, pp. 73–8.
- [22] MILL B.V., BUTASHIN A.V., ELLERN A.M., MAJER A.A., *Phase formation in the CaO–Ga₂O₃–GeO₂ system*, Inorganic Materials **17**(9), 1981, pp. 1216–20; (original: Izvestiya Akademii Nauk SSSR, Neorganicheskie Materialy **17**(9), 1981, pp. 1648–53).
- [23] PADLYAK B.V., BUCHYNSKII P.P., Patent of Ukraine, No. UA 25235 A, October 30, 1998.
- [24] RAMOS F., LORO H., CAMARILLO E., GARCÍA SOLÉ J., KAMINSKII A.A., CALDIÑO U.G., *Optical absorption spectroscopy of Nd³⁺ in the Ca₃Ga₂Ge₃O₁₂ laser garnet crystal*, Optical Materials **12**(1), 1999, pp. 93–7.
- [25] CALDIÑO U.G., VODA M., JAQUE F., GARCÍA SOLÉ J., KAMINSKII A.A., *Nd³⁺ multisites in the disordered Ca₃Ga₂Ge₃O₁₂ laser crystal*, Chemical Physics Letters **213**(1–2), 1993, pp. 84–8.
- [26] JAQUE D., CALDIÑO U.G., ROMERO J.J., GARCÍA SOLÉ J., *Fluorescence dynamics and laser properties of the Nd³⁺:Ca₃Ga₂Ge₃O₁₂ crystal*, Journal of Luminescence **83–84**, 1999, pp. 477–9.
- [27] KAMINSKII A.A., BELOKONEVA E.L., MILL B.V., PISAREVSKII YU.V., SARKISOV S.E., SILVESTROVA I.M., BUTASHIN A.V., KHODZHABAGYAN G.G., *Pure and Nd³⁺-doped Ca₃Ga₂Ge₄O₁₄ and Sr₃Ga₂Ge₄O₁₄ single crystals, their structure, optical, spectral luminescence, electromechanical properties, and stimulated emission*, Physica Status Solidi A **86**(1), 1984, pp. 345–62.
- [28] PADLYAK B., VLOKH O., RYBA-ROMANOWSKI W., LISIECKI R., *Optical spectroscopy of Nd³⁺ centres in the glass with 3CaO–Ga₂O₃–3GeO₂ composition*, Ukrainian Journal of Physical Optics **7**(4), 2006, pp. 149–58.
- [29] PADLYAK B., MUDRY S., HALCHAK V., KOROLYSHYN A., RYBICKI J., WITKOWSKA A., *Structure of CaO–Ga₂O₃–GeO₂ glasses: X-ray and molecular dynamics simulation studies*, Optica Applicata **30**(4), 2000, pp. 691–9.

- [30] CHELSTOWSKI D., WITKOWSKA A., RYBICKI J., PADLYAK B., TRAPANANTI A., PRINCIPI E., *EXAFS study of glasses of the CaO–Ga₂O₃–GeO₂ system*, *Optica Applicata* **33**(1), 2003, pp. 125–32.
- [31] WITKOWSKA A., PADLYAK B., RYBICKI J., *Influence of rare-earth impurities on the Ge and Ga local structure in the Ca₃Ga₂Ge₃O₁₂ glass*, *Journal of Non-Crystalline Solids* **352**(40–41), 2006, pp. 4346–50.
- [32] WITKOWSKA A., PADLYAK B., RYBICKI J., *An EXAFS study of the local structure of rare-earth luminescence centres in the 3CaO–Ga₂O₃–3GeO₂ glass*, *Optical Materials* **30**(5), 2008, pp. 699–702.
- [33] CARNALL W.T., FIELDS P.R., RAJNAK K., *Electronic energy levels in the trivalent lanthanide aquo ions. I. Pr³⁺, Nd³⁺, Pm³⁺, Sm³⁺, Dy³⁺, Ho³⁺, Er³⁺, and Tm³⁺*, *Journal of Chemical Physics* **49**(10), 1968, pp. 4424–42.
- [34] HENDERSON B., BARTRAM R.H., *Crystal-Field Engineering of Solid-State Lasers Materials*, Cambridge University Press, Cambridge 2000.
- [35] PECORARO E., SAMPAIO J.A., NUNES L.A.O., GAMA S., BAESSO M.L., *Spectroscopic properties of water free Nd₂O₃-doped low silica calcium aluminosilicate glasses*, *Journal of Non-Crystalline Solids* **277**(2–3), 2000, pp. 73–81.
- [36] COURROL L.C., KASSAB L.R.P., CACHO V.D.D., TATUMI S.H., WETTER N.U., *Lead fluoroborate glasses doped with Nd³⁺*, *Journal of Luminescence* **102–103**, 2003, pp. 101–5.
- [37] SENE F.F., MARTINELLI J.R., GOMES L., *Optical and structural characterization of rare earth doped niobium phosphate glasses*, *Journal of Non-Crystalline Solids* **348**, 2004, pp. 63–71.
- [38] PARDO J.A., PEÑA J.I., MERINO R.I., CASES R., LARREA A., ORERA V.M., *Spectroscopic properties of Er³⁺ and Nd³⁺ doped glasses with the 0.8CaSiO₃–0.2Ca₃(PO₄)₂ eutectic composition*, *Journal of Non-Crystalline Solids* **298**(1), 2002, pp. 23–31.
- [39] RAPP C.F., *Laser glasses*, [In] *Handbook of Lasers Sciences and Technology*, [Ed.] M.J. Weber, Optical Materials, Part 3, Vol. V, CRC Press, Boca Raton (FL) 1987.
- [40] JUDD B.R., *Optical absorption intensities of rare-earth ions*, *Physical Review* **127**(3), 1962, pp. 750–61.
- [41] OFELT G.S., *Intensities of crystal spectra of rare-earth ions*, *Journal of Chemical Physics* **37**(3), 1962, p. 511.
- [42] KUMAR G.A. DE LA ROSA-CRUZ E. MARTINEZ A., UNNIKISHNAN N.V., UEDA K., *Influence of borate content on the radiative properties of Nd³⁺ ions in fluorophosphate glasses*, *Journal of the Physics and Chemistry of Solids* **64**(1), 2003, pp. 69–76.
- [43] D'ACAPITO F., MOBILIO S., GASTALDO P., BARBIER D., SANTOS L.F., MARTINS O., ALMEIDA R.M., *Local order around Er³⁺ ions in SiO₂–TiO₂–Al₂O₃ glassy films studied by EXAFS*, *Journal of Non-Crystalline Solids* **293–295**, 2001, pp. 118–24.
- [44] WADA N., KOJIMA K., OZUTSUMI K., *Memoirs of the SR Center, Ritsumeikan University*, No. 7, 2005, p. 5.

Received September 18, 2007
in revised form January 4, 2008