

Optical spectroscopy of the Ho-doped glasses with $3\text{CaO-Ga}_2\text{O}_3-3\text{GeO}_2$ composition

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The UV and visible optical spectra (absorption, emission and luminescence excitation) of the Ho-doped $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$ glasses at room and liquid nitrogen temperatures have been investigated for the first time. The Ho-doped ($C_{\text{Ho}} = 0.7$ wt%) glass samples with garnet $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ (or $3\text{CaO-Ga}_2\text{O}_3-3\text{GeO}_2$) composition were prepared by the conventional high-temperature synthesis technique. By optical and EPR spectroscopy it has been shown that the holmium impurity is incorporated into the glass network as Ho^{3+} ($4f^{10}, {}^5I_8$) ions, exclusively. All transitions of the Ho^{3+} ions observed in optical spectra of Ho-doped $3\text{CaO-Ga}_2\text{O}_3-3\text{GeO}_2$ glasses are identified. The Ho^{3+} optical absorption spectrum has been analyzed and described in the framework of Judd-Ofelt theory. Optical absorption and emission spectra of the Ho^{3+} ions in the $3\text{CaO-Ga}_2\text{O}_3-3\text{GeO}_2$ glasses are quite similar to Ho^{3+} optical spectra in other oxide glasses and are characterized by statistical distribution of the local crystal field parameters. Incorporation peculiarities and spectroscopic properties of Ho^{3+} impurity ions in the glasses of $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$ system are discussed.

Keywords: $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$ glass, Ho^{3+} ion, optical absorption, luminescence, inhomogeneous broadening.

1. Introduction

Disordered crystals and glasses doped with rare-earth and transition metal ions are still attractive as a possible laser media for solid state lasers, operating in the visible and infrared spectral region. It also concerns the Ho-doped complex oxide crystals and glasses, because the Ho^{3+} ions in these compounds exhibit the eye-safe potential laser emission even at room temperature with a low threshold action [1]–[3]. Moreover, within the Ho^{3+} energy level scheme several up-conversion processes can take place resulting in the visible anti-Stokes luminescence [4].

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The glasses and crystals of $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$ system and other compounds with close chemical composition and structure, doped with rare-earth and transition metal ions represent perspective materials for solid state lasers and other applications in optoelectronics. Particularly, the $\text{Ca}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}$ garnet host crystals co-doped with Ho^{3+} and Tm^{3+} represent new potential laser material for the 2 μm region [5]. In contrast to crystals optical properties, peculiarities of incorporation and ligand field for holmium impurity ions in complex oxide glasses are studied insufficiently.

In $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$ ternary system exist three stable crystalline forms: $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ (ordered garnet structure, space group – $Ia3d$), $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ (substitutionally disordered Ca-gallogermanate structure, space group – $P321$), $\text{Ca}_2\text{Ga}_2\text{GeO}_7$ (gelenite structure, space group – $P\bar{4}2_1m$) [6], [7] and corresponding glassy (or vitreous) forms with similar to the crystals stoichiometric composition [8]. At present the high quality glasses with garnet $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ (or $3\text{CaO-Ga}_2\text{O}_3\text{-3GeO}_2$) composition doped with rare-earth metal (Eu, Ho, Nd, Ce, Er) ions have been obtained. Results of spectroscopic studies of the Eu-doped $3\text{CaO-Ga}_2\text{O}_3\text{-3GeO}_2$ glasses firstly were presented in [9], [10]. Up to now optical and EPR spectra of the Ho-doped glasses and crystals of $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$ system have not been investigated.

In this paper, the optical studies of the Ho-doped glasses with $3\text{CaO-Ga}_2\text{O}_3\text{-3GeO}_2$ composition in the UV and visible spectral region have been presented for the first time.

2. Experimental

The Ho-doped glasses of high chemical purity and optical quality with $3\text{CaO-Ga}_2\text{O}_3\text{-3GeO}_2$ compositions were obtained in corundum crucibles by high-temperature synthesis according to [8]. Chemical composition of the obtained samples was controlled by the X-ray microanalysis technique using a Camebax apparatus. The holmium impurity was added to the glass composition as Ho_2O_3 compound in amounts 0.7 wt%. The obtained Ho-doped glasses were characterized by lightly yellow color.

The Ho-doped glasses with $3\text{CaO-Ga}_2\text{O}_3\text{-3GeO}_2$ composition show typical glassy-like X-ray structure factor similar to the structure factor obtained for undoped glasses of the same composition [11]. Preliminary results of structural studies of the undoped glasses of $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$ system with different compositions by extended X-ray absorption fine structure technique are presented in [12].

Optical absorption spectra were registered at room temperature on a Specord M-40 (Carl Zeiss Jena) spectrophotometer. Photoluminescence spectra were measured at temperatures 300 and 85 K upon frontal excitation and observation of the sample emission using equipment built in the Condensed Matter Spectroscopy Division (Institute of Experimental Physics, Gdańsk University, Poland). The emission spectra were corrected for the spectral sensitivity of the equipment. As excitation source was used a Hanovia xenon lamp ($P = 1000$ W). The wavelengths required for excitation and observation were selected using an SPM-2 prismatic monochromator (Carl Zeiss Jena) with stepping motors driven by a computer and photomultipliers used in the

detection branch and working in analog or photon counter regime. In the latter case they send data to the computer *via* a digital boxcar system. A Hamamatsu R 928 photomultiplier was used as a detector. Samples for optical measurements were cut and polished to the approximate size of $8 \times 4 \times 3 \text{ mm}^3$.

3. Results and discussion

The Ho impurity in the oxide compounds can be revealed as Ho^{3+} ($4f^{10}, {}^5I_8$) and Ho^{2+} ($4f^{11}, {}^4I_{15/2}$) ions with characteristic optical and EPR spectra. The X-band EPR spectra of the Ho^{3+} and Ho^{2+} ions in the oxide crystals and glasses are observed at liquid helium temperatures only and can be described by spin Hamiltonian of axial symmetry with effective electron spin $S_{\text{eff}} = 1$ and $S_{\text{eff}} = 1/2$, respectively [13]. In the Ho-doped glasses with $3\text{CaO-Ga}_2\text{O}_3-3\text{GeO}_2$ composition the Ho^{3+} EPR spectrum was observed at liquid helium temperatures [14]. The EPR spectrum of Ho^{2+} ions was not detected even at $T = 4.2 \text{ K}$, what means that the holmium impurity is incorporated into $3\text{CaO-Ga}_2\text{O}_3-3\text{GeO}_2$ glass network as Ho^{3+} , exclusively.

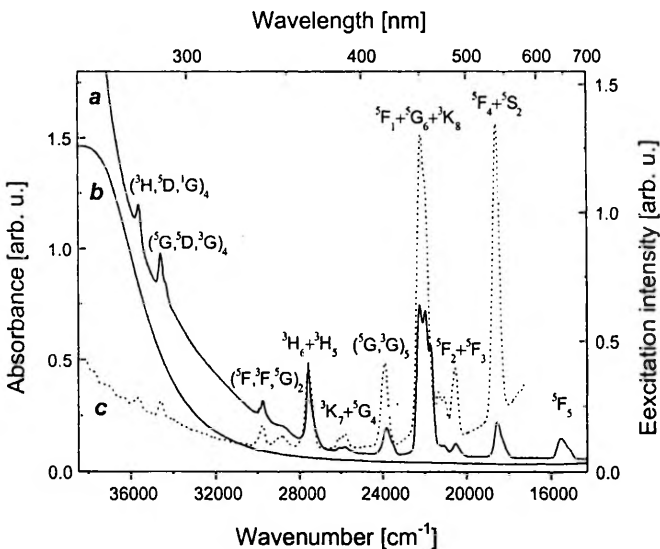


Fig. 1. Optical absorption (curves *a*, *b*) and luminescence excitation ($\lambda_{\text{obs}} = 610 \text{ nm}$) (curve *c*) spectra of the Ho-doped (*a*, *c*) and undoped (*b*) glasses with $3\text{CaO-Ga}_2\text{O}_3-3\text{GeO}_2$ composition, registered at $T = 295 \text{ K}$.

Optical absorption spectrum of the Ho-doped glasses with $3\text{CaO-Ga}_2\text{O}_3-3\text{GeO}_2$ composition in the $270\text{--}700 \text{ nm}$ ($14000\text{--}38000 \text{ cm}^{-1}$) spectral range consists of several absorption bands with weakly resolved structure at room temperature (Fig. 1, curve *a*). One can notice that the undoped glasses of $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$ system are transparent in UV region up to $280\text{--}300 \text{ nm}$ (Fig. 1, curve *b*) and are characterized by high transparency in the IR spectral range [8]. In accordance with [5], [15], all observed

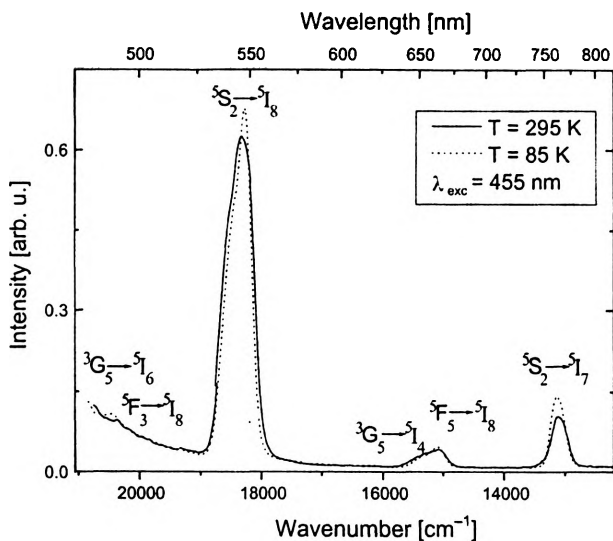


Fig. 2. Photoluminescence spectra of the Ho-doped glasses with $3\text{CaO-Ga}_2\text{O}_3-3\text{GeO}_2$ composition, registered at $T = 295\text{ K}$ and $T = 85\text{ K}$.

absorption lines (Fig. 1, curve *a*) are assigned to appropriate electronic $f-f$ -transitions of the Ho^{3+} ions, in general, from 5I_8 ground state to different excited states. Any bands, characteristic of Ho^{2+} ions [16] were not observed in the optical absorption spectra that confirm incorporation of holmium impurity into the $3\text{CaO-Ga}_2\text{O}_3-3\text{GeO}_2$ -glass network in the Ho^{3+} valence state. The assignment of the multiplets is complicated because at room temperature the Stark components of the 5I_8 ground state are populated and because a high number of excited levels, which are very close one to another, is involved in the absorption transitions. Moreover, the inhomogeneous broadening of the Ho^{3+} optical bands connected with disordering of the glass structure has been revealed also. In result, most of the observed complexes and weakly resolved bands can only be assigned to groups of absorption transitions as showed in Fig. 1, curve *a*.

The transition energies and relative intensity of absorption lines for Ho^{3+} ions in the $3\text{CaO-Ga}_2\text{O}_3-3\text{GeO}_2$ glasses are close to those measured for other Ho-doped glasses [1]–[4], [17] and crystals [5], [16] and can be described by Judd–Ofelt theory [18], [19]. Theoretical evaluation of the energies of absorption bands E , the oscillator strength f , the Judd–Ofelt intensity parameters $\Omega_{2,4,6}$ and spectroscopic quality factor Ω_4/Ω_6 show satisfactory agreement with the same parameters, obtained from experimental Ho^{3+} transitions in the $3\text{CaO-Ga}_2\text{O}_3-3\text{GeO}_2$ glasses.

In the luminescence excitation spectra of the Ho-doped glasses with $3\text{CaO-Ga}_2\text{O}_3-3\text{GeO}_2$ composition the number of unresolved and weakly resolved bands were observed (Fig. 1, curve *c*), which show good correlation with optical absorption transitions (Fig. 1, curve *a*). The Ho^{3+} emission spectra in the visible (400–800 nm) spectral range, obtained under different excitation at room and liquid nitrogen temperatures are presented in the Figs. 2 and 3. Emission spectra consist of several

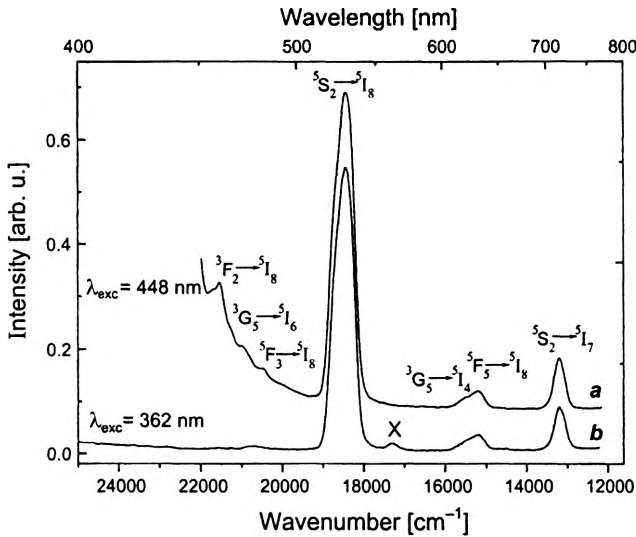


Fig. 3. Luminescence spectra of the Ho-doped $3\text{CaO-Ga}_2\text{O}_3\text{-3GeO}_2$ glasses excited with $\lambda_{\text{exc}} = 448$ nm (curve *a*) and $\lambda_{\text{exc}} = 362$ nm (curve *b*) and registered at $T = 85$ K.

lines that belong to different transitions of the Ho^{3+} ions, assignment of which is given in the Figs. 2–3. No better resolution of the Ho^{3+} lines in emission spectra was observed at liquid nitrogen temperatures (Fig. 2), which is the evidence of inhomogeneous broadening of the spectral lines. The visible light leads to excitation of Ho^{3+} luminescence only, and clearly all lines in excitation spectra reveal at $\lambda_{\text{exc}} = 448$ nm (see Fig. 2 and Fig. 3, curve *a*). At excitation in the UV region ($\lambda_{\text{exc}} = 362$ nm) in the emission spectrum an additional weak band X with maximum about 550 nm was observed (Fig. 3, curve *b*). This band cannot be explain in the framework of Ho^{3+} transitions and cannot be assigned to UV-induced intrinsic broad band luminescence, which was observed in the undoped glasses of $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$ system [20] and needs additional study.

One can notice that optical absorption and luminescence spectra of the Ho^{3+} in the glasses of $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$ system are almost independent of basic glass composition and temperature in the 85–300 K range and are typical of Ho-doped oxide glasses and crystals [1]–[5]. Best resolution of Ho^{3+} absorption and luminescence spectra was observed in crystals particularly, in the $\text{Ca}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}$ garnet [5]. The significant inhomogeneous broadening of the Ho^{3+} spectral lines in the $3\text{CaO-Ga}_2\text{O}_3\text{-3GeO}_2$ glasses in comparison with $\text{Ca}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}$ crystals is related to substitutional disorder and continual disturbance of the short-range order, characteristic of glass network. Therefore, in the glasses we can consider the ensemble of Ho^{3+} luminescence centers with slightly different local environment and statistically distributed crystal field parameters. On the basis of similarity of Ho^{3+} spectra and local structure of the $3\text{CaO-Ga}_2\text{O}_3\text{-3GeO}_2$ (or $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$) glasses and $\text{Ca}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}$ garnet crystals we can suppose that Ho^{3+} ions are localized in the sites with eight-fold co-ordination.

The rare-earth luminescence centers with different local environment in the glass network can be resolved by fluorescence line narrowing spectroscopy. Detailed studies of local steric structure for different Ho^{3+} centers in the glasses of $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$ system will be a subject of future work.

4. Conclusions

Based on results of investigations the following conclusions can be drawn:

1. The holmium impurity is incorporated into the $3\text{CaO-Ga}_2\text{O}_3\text{-3GeO}_2$ glass network as Ho^{3+} ($4f^{10}$, 5I_8) ions, exclusively, because the optical and EPR spectra of the Ho^{2+} ($4f^{11}$, $^5I_{15/2}$) were not registered.

2. All transitions of the Ho^{3+} ions, observed in optical spectra of the Ho-doped $3\text{CaO-Ga}_2\text{O}_3\text{-3GeO}_2$ glasses, are identified. The Ho^{3+} optical absorption spectra can be analyzed and described in the framework of Judd-Ofelt theory for centers with statistically distributed crystal field parameters.

3. Optical spectra of the Ho^{3+} ions in the $3\text{CaO-Ga}_2\text{O}_3\text{-3GeO}_2$ glasses are quite similar to Ho^{3+} optical spectra for other oxide glasses and are characterized by inhomogeneous broadening caused by structural disordering of the glass structure.

4. The rare-earth ions (particularly the Ho^{3+} and Eu^{3+}) lead to disappearing of the intrinsic luminescence characteristic of the undoped glasses of the $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$ system, because this broad band luminescence in the Ho- and Eu-doped (amount of the Ho and Eu impurities equals 0.7 wt%) glasses was not observed.

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