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OPTICAL PROPERTIES OF THE $Ag_{28}Ga_{28}Ge_{532}Er_2S_{1123}$ AND $Ag_{12}Ga_{12}Ge_{228}Er_2S_{483}$ GLASSES

Absorption spectra of the glasses Ag28Ga28Ge532Er2S1123 and Ag12Ga12Ge228Er2S483 in the 450–1050 nm range at room temperature were investigated. PL bands with maxima at 980 and 1540 nm were recorded under laser excitation with 800 nm wavelength. PL emission mechanism is analyzed from energy transfer processes, taking into account partial cluster formation of erbium ions and energy transition diagram of Er3+.

Keywords: absorption spectra, photoluminescence, erbium ion, cluster formation, emission mechanism.

1. INTRODUCTION

Over the past two decades, substantial research interest was attracted to the study of the optical properties of semiconductors doped with rare-earth metals (RE). This is due to the growing needs of the industry in optoelectronic devices operating in the spectral range compatible with telecommunication gadgets. The most commonly used RE is erbium that has an intensive emission band near 1.5 μm and low energy losses in fiber optics at this wavelength. Additionally, erbium-doped crystalline and amorphous materials can be used as active media in laser technology [1], displays, optical amplifiers, photonic devices [2], non-contact temperature [3, 4] and g-irradiation sensors [5, 6, 7].

Phase equilibria in the reciprocal system $AgGaS_2$ + $GeSe_2$ Û $AgGaSe_2$ + GeS_2 were investigated, and the glass formation region was determined [8]. An alloy with the composition $Ag_{0.05}Ga_{0.05}Ge_{0.95}S_2$ is characterized by the largest transparency window in this system. It was doped with 0.18 and 0.42 mol.% Er_2S_3 (samples $Ag_{28}Ga_{28}Ge_{532}Er_2S_{1123}$ and $Ag_{12}Ga_{12}Ge_{228}Er_2S_{483}$, respectively).

In our previous works on these glasses, we investigated the main structural units of the glass-forming matrix by Raman spectroscopy, as well as photoluminescence spectra under excitation by 532 and 980 nm wavelengths [4, 9]. Partial clustering of erbium ions was established from EPR and static magnetization studies, and the effect of g-irradiation on glass photoluminescence was analyzed [5].

The objective of this work is to investigate the absorption spectra and the mechanism of PL emission under laser excitation at 800 nm wavelength.

2. EXPERIMENTAL

The alloys were synthesized from elemental components (Ag, Ga, Ge, Se – 99.997 wt.% purity, S, 99.999 wt.%, Er, 99.9 wt.%) in evacuated thin-walled quartz ampoules in two stages. To prevent condensation losses of the vapor phase, the free volume of the container

was thermostated with asbestos cord. The residual pressure in ampoules was 0.1 Pa. Initially, the ampoules were heated in oxygen-gas burner flame for the binding of elemental sulfur. Then they were placed in a shaft-type furnace and heated at a rate of 20 K/hr to the maximum temperature of 1273 K. After holding at this temperature for 10 hours, the alloys were quenched into 25% aqueous saline solution at room temperature. The glassy state of the alloys was examined by X-ray diffraction at a DRON 4-13 diffractometer, CuKα radiation (Fig. 1).

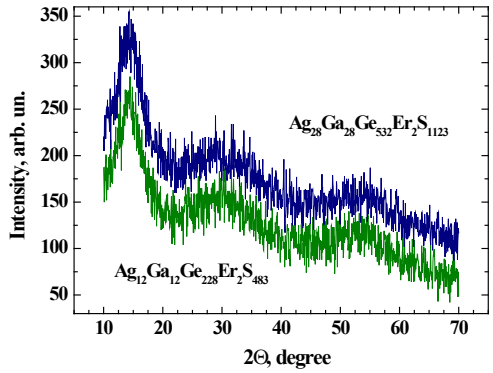

Fig. 1. X-ray diffraction patterns of the glasses.

The study of absorption spectra and photoluminescence utilized an MDR-206 monochromator with Si and PbS photodetectors. Luminescence excitation was performed by a laser at 800 nm wavelength and 400 mW power. The photoluminescence signal was received from the same sample surface as the excitation. The sample thickness was 0.5 mm.

3. RESULTS AND DISCUSSION

The absorption spectra of glasses were investigated at room temperature in the 450–1050 nm range (Fig. 2). The recorded absorption bands with maxima at 520, 550, 660, 805, and 980 nm correspond to the transitions in the *f*-shell of Er^{3+} ions from the ground state to the excited states $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$, respectively. The intensity of the absorption bands increases with erbium content, while their position does not change. We established in a previous work [9] that the absorption coefficient decreases with the increase in erbium concentration. This is due to the structural ordering of glass and, as it follows from Raman spectroscopy studies, to the decrease in the number of structural units $[S_3Ge(Ga)–(Ga)GeS_3]$ and the increase of the $[Ge(Ga)S_4]$ units.

The photoluminescence spectra (PL) of glasses in the 600–2000 nm range were investigated at room temperature under excitation by 800 nm wavelength (Figs. 3, 4). Two maxima at about 980 and 1540 nm were recorded in the near infrared spectral region.

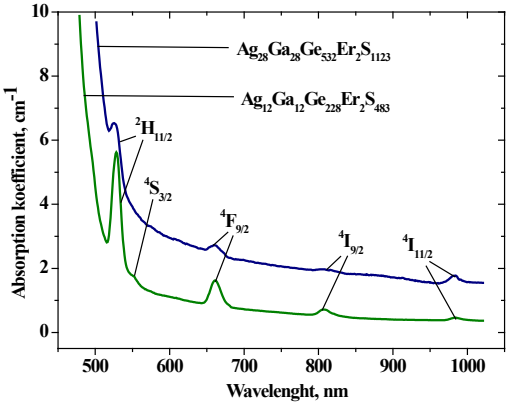

Fig. 2. Absorption spectra of the glasses at room temperature.

The emission efficiency of the band at 1540 nm wavelength is important for the use in telecommunication devices. A parameter of the effective bandwidth ($\Delta\lambda_{eff}$) is used since the band is asymmetrical. It is calculated by the formula [10]:

$$\Delta\lambda_{eff} = \frac{\int I(\lambda)d\lambda}{I_{max}} \qquad (1)$$

where I(λ) is the emission intensity at wavelength λ; I_{max} is the maximum emission intensity.

The calculated $\Delta\lambda_{eff}$ values for the glasses are 63 and 66 nm for $Ag_{28}Ga_{28}Ge_{532}Er_2S_{1123}$ and $Ag_{12}Ga_{12}Ge_{228}Er_2S_{483}$, respectively. Clearly, not only PL intensity increases with erbium content but also does the effective width of the emission band. Additionally, the $\Delta\lambda_{eff}$ values for the excitation at 800 nm is higher for these glasses than for the 980 nm excitation [11].

In our previous work [9], the excitation of these samples by 980 nm wavelength yielded in the visible range a green (520 nm) and a red (660 nm) PL band. However, no PL was detected in the visible spectral range when excited by 800 nm wavelength.

This is due to the fact that anti-Stokes PL (under 980 nm excitation) is associated with the absorption of two photons by Er^{3+} ions which are promoted from the ground state $^4I_{15/2}$ to the excited state $^4F_{7/2}$ ($^4I_{15/2} + hn_{980} \rightarrow {}^4I_{11/2} + hn_{980} \rightarrow {}^4F_{7/2}$) with subsequent non-radiative relaxation to the state $^2H_{11/2}$. Since

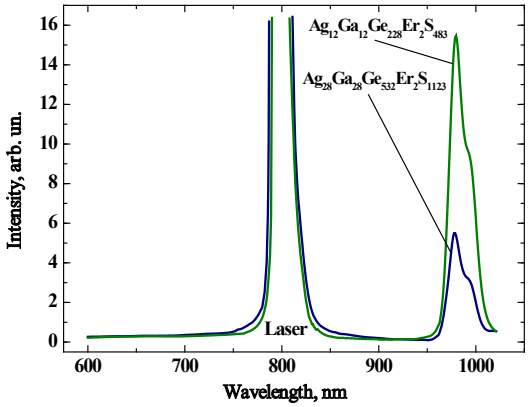

Fig. 3. PL spectra of the glasses excited with 800 nm laser (600–1050 nm range).

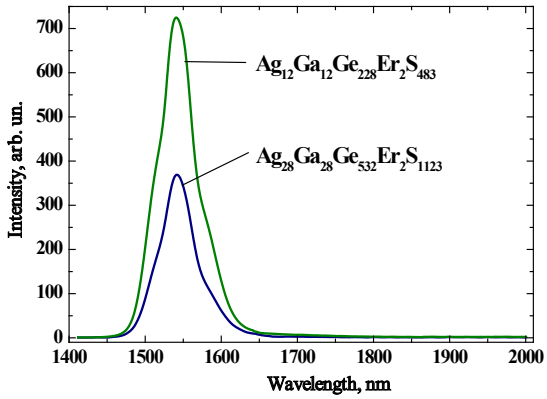

Fig. 4. PL spectra of the glasses excited with 800 nm laser (1400–2000 nm range).

the excitation at 800 nm has higher energy compared to 980 nm, the absorption of two photons promotes erbium ions to the excited state $^2H_{9/2}$ ($^4I_{15/2} + hn_{800} \rightarrow {}^4I_{9/2} + hn_{800} \rightarrow {}^2H_{9/2}$) located above the absorption edge (Fig. 2) in the conduction band.

The emission mechanism in these glasses can be determined from the transition chart for Er^{3+} ions (Fig. 5). Erbium ions in the state $^4I_{13/2}$ are promoted due to absorption of 800 nm photons or energy transfer (ET) from adjacent ions in the state $^4I_{9/2}$ to the state $^2H_{11/2}$. These erbium ions can non-radiatively relax to the state $^4S_{3/2}$. However, erbium ions can not relax non-radiatively to lower energy states because of the large energy gap and low phonon energy (about 300-400 cm^{-1} [9]). Excited states $^4I_{11/2}$ and $^4I_{13/2}$ which yield PL bands with maxima at 980 and 1540 nm result from cross-relaxation CR_1, CR_2 (Fig. 5):

$$^2H_{11/2} + {}^4I_{15/2} \rightarrow {}^4I_{9/2} + {}^4I_{13/2} \quad (2)$$

$$^2H_{11/2} + {}^4I_{13/2} \rightarrow {}^4F_{9/2} + {}^4I_{11/2} \quad (3)$$

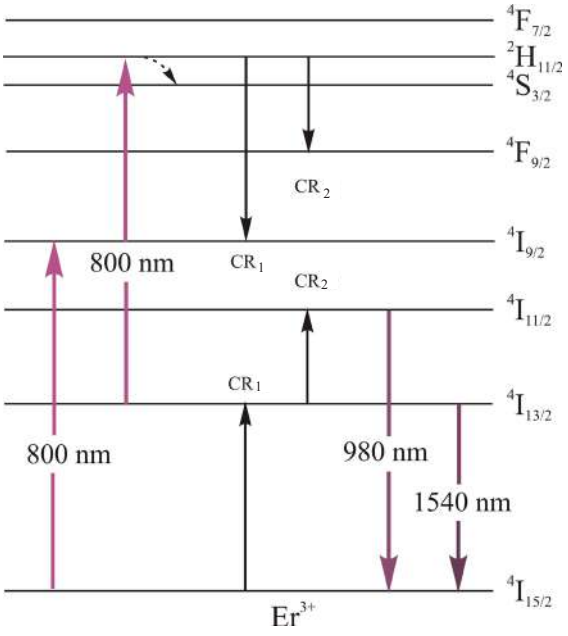

Fig. 5. Diagram of energy levels in Er^{3+} ions.

Therefore, an important role in the PL mechanism is played by the energy exchange (ET or CR) between the neighboring Er^{3+} ions. Such processes are typical of erbium ions which are involved in the formation of clusters [12]. It was established in our previous work [5] that clusters of up to 10^3 erbium ions form in the $Ag_{0.05}Ga_{0.05}Ge_{0.95}S_2$–$Er_2S_3$ glasses.

4. CONCLUSIONS

Absortion spectra in the glasses $Ag_{28}Ga_{28}Ge_{532}Er_2S_{1123}$ and $Ag_{12}Ga_{12}Ge_{228}Er_2S_{483}$ were investigated. Recorded absorption bands with maxima at 520, 550, 660, 805, 980 nm correspond to the transitions in 4f intra-shell transitions from the ground state to the excited states $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$, respectively. Stokes PL with maxima at 980 and 1540 nm was recorded upon laser excitation at 800 nm wavelength. A model explaining PL emission mechanism was elucidated from the energy level diagram of Er^{3+} ions.

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Absorption spectra of the glasses $Ag_{28}Ga_{28}Ge_{532}Er_2S_{1123}$ and $Ag_{12}Ga_{12}Ge_{228}Er_2S_{483}$ in the 450–1050 nm range at room temperature were investigated. PL bands with maxima at 980 and 1540 nm were recorded under laser excitation with 800 nm wavelength. PL emission mechanism is analyzed from energy transfer processes, taking into account partial cluster formation of erbium ions and energy transition diagram of Er^{3+}.

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ОПТИЧНІ ВЛАСТИВОСТІ СТЕКОЛ $Ag_{28}Ga_{28}Ge_{532}Er_2S_{1123}$ ТА $Ag_{12}Ga_{12}Ge_{228}Er_2S_{483}$

Досліджено спектри поглинання стекол $Ag_{28}Ga_{28}Ge_{532}Er_2S_{1123}$ та $Ag_{12}Ga_{12}Ge_{228}Er_2S_{483}$ в діапазоні 450 – 1050 нм за кімнатної температури. Зафіксовано смуги ФЛ із максимумами 980 та 1540 нм при збудженні лазером із довжиною хвилі 800 нм. На основі процесів обміну енергією, враховуючи часткову кластеризацію іонів Ербію та діаграму енергетичних переходів в іонах Er^{3+}, проаналізовано механізм випромінювання ФЛ.

Ключові слова: спектр поглинання, фотолюмінесценція, іон Ербію, кластеризація, механізм випромінювання.

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В. В. Галян, И. Д. Олексеюк, И. А. Иващенко, А. Г. Кевшин, П. В. Тищенко, М. В. Шевчук

ОПТИЧЕСКИЕ СВОЙСТВА СТЕКОЛ $Ag_{28}Ga_{28}Ge_{532}Er_2S_{1123}$ И $Ag_{12}Ga_{12}Ge_{228}Er_2S_{483}$

Исследованы спектры поглощения стекол $Ag_{28}Ga_{28}Ge_{532}Er_2S_{1123}$ и $Ag_{12}Ga_{12}Ge_{228}Er_2S_{483}$ в диапазоне 450 – 1050 нм при комнатной температуре. Зафиксировано полосы ФЛ с максимумами 980 и 1540 нм при возбуждении лазером с длиной волны 800 нм. На основе процессов обмена энергией, учитывая частичную кластеризацию ионов эрбия и диаграмму энергетических переходов в ионах Er^{3+}, проанализирован механизм излучения ФЛ.

Ключевые слова: спектр поглощения, фотолюминесценция, ион эрбия, кластеризация, механизм излучения.