ISSN 2616-8685. JOURNAL OF PHYSICS AND ELECTRONICS Vol. 27(1), 2019
DOI 10.15421/331909

EFFECT OF IMPURITIES AND DISORDERING ON THE PHOTOLUMINESCENCE OF CRYSTALS AND GLASSES IN THE SYSTEM Li_2O - $7GeO_2$

O.V. Ohiienko*, V.N. Moiseienko, M.D. Volnyanskij

Oles Honchar Dnipro National University, Dnipro, Ukraine
**e-mail: kombi21251@outlook.com*

The work is devoted to the study of photoluminescence spectra of weakly polar ferroelectric crystals $Li_2Ge_7O_{15}$ and Li_2O – $7GeO_2$ glasses. For all initial samples was observed the wide intensive luminescence band with maximum in the region of 525–550nm. The spectral distribution of intensity and the position of the maximum of the band for a $Li_2Ge_7O_{15}$ crystal depended on the excitation wavelength (λ_{ex}=405 nm or 365nm were used). The spectral profile of the luminescence band was broadened in glass containing of 0.67% copper. The intensity of the luminescence band was decreased 6 times for glass doped with Cr^{3+} ions (0.01%) as compared with glass containing Cu^{2+} ions. The intense luminescence band of Cr^{3+} ions with λ_{max}=659nm was appeared starting from 600. The assumption about the nature of the broad luminescence band observed in both nominally pure and doped glasses and crystals was made: the source of luminescence can be germanium - oxygen complexes [GeO_4] and [GeO_6] of the tetrahedral and octahedral configuration in the material structure.

Keywords: photoluminescence spectrum, lithium germanate, crystals, glasses, own glow center, germanium - oxygen complexes, impurity luminescent centers, $Cr^{3+}$and Cu^{2+} impurity ions.

Received 05.09.2019; Received in revised form 11.10.2019; Accepted 15.10.2019

1. Introduction

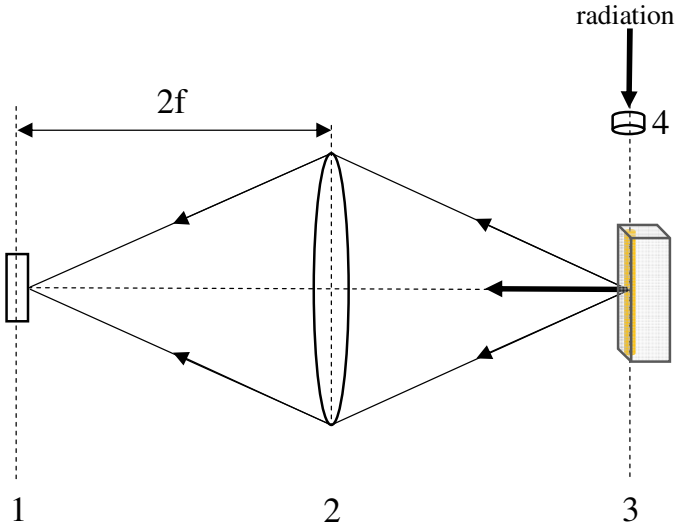
The interests to luminescent materials caused by their important applied application as an effective luminophores and scintillators. For example, bismuth germanate crystals with eulitine structure are ones of effective materials for scintillators which having own luminescence centrum and don't need to inject additional emission centers. In the system Bi_2O_3–GeO_2 are possibility to formation stable or metastable crystals phases among which $Bi_{12}GeO_{20}$ and $Bi_2Ge_3O_9$ phases [1]. These materials are of interest from fundamental point view to establish the nature of their own luminescence centers. In the paper [1] it was established that luminescence in $Bi_4Ge_3O_{12}$, $Bi_{12}GeO_{20}$, $Bi_2Ge_3O_9$ materials and Bi_2O_3 of the cubic δ-modification is due to radiative transitions in structural complexes containing Bi^{3+} ions and the nearest oxygen environment. In addition, the thermoluminescence band in $Bi_4Ge_3O_{12}$, $Bi_{12}GeO_{20}$ and $Bi_4Ge_3O_{12}$ with a maximum at 143 K was associated with defects in the germanium sublattice.

In this work we are chosen a materials which have own photoluminescence in the visible region of the spectrum [2] and can serve as a matrix for impurity luminescence [3]. The general regularity of the considered materials is that they have oxygen as one of the main structure-forming elements, which participates in the formation of the material structure, forming oxygen-containing centers and plays an active role in luminescent processes [4-6]. The investigations of glass structure in the system Li_2O – $7GeO_2$ and crystals $Li_2Ge_7O_{15}$ by Raman spectroscopy [7] allowed establishing that the short range and middle-range orders in the initial uniform glass correspond to the structural motive of the crystal. Phase separation occurred during further heat treatment of glass with the formation of inhomogeneities with the Li_2O – $4GeO_2$ structure. The present work is devoted to the study of the influence of disordering and additionally introduced impurity centers on the photoluminescence spectra of glasses and crystals in the system Li_2O – $7GeO_2$ in the visible range of the spectrum in connection with intrinsic luminescence centers with the aim of elucidating their nature.

2. Experiment

Measurement of luminescence spectra was performed with the spectrometer based on DFS-12. The photoluminescence spectra were registered using FEU-79 photoelectronic

multiplier in the range from 450 nm to 650 nm. The photoluminescence spectra were excited by a semiconductor laser with λ_{ex}=405 nm and LED with λ_{ex}=365 nm. Figure 1 shown the geometry of photoluminescence measurement. The luminescence spectra of all studied samples were measured under the same conditions in 90-degree geometry.



1 – spectrometer based on DFS-12, 2 – lens, 3 – sample, 4 – beam collimator
Fig. 1. The geometry of measurement photoluminescence (from the side view)

The luminescence spectra were decomposed into elementary spectral components using the Origin Pro software package. For each spectrum, the positions of intensity maximum were determined. The spectral profile was approximated by several Gaussian functions of the following form:

$$y = y_0 + \frac{A \exp\left[\frac{-4\ln(2)(x - x_c)^2}{\omega^2}\right]}{\omega\sqrt{\frac{\pi}{4\ln(2)}}}$$

y_0– low level, A – area under the curve, x_c – center of maximum, ω – peak width at half height.

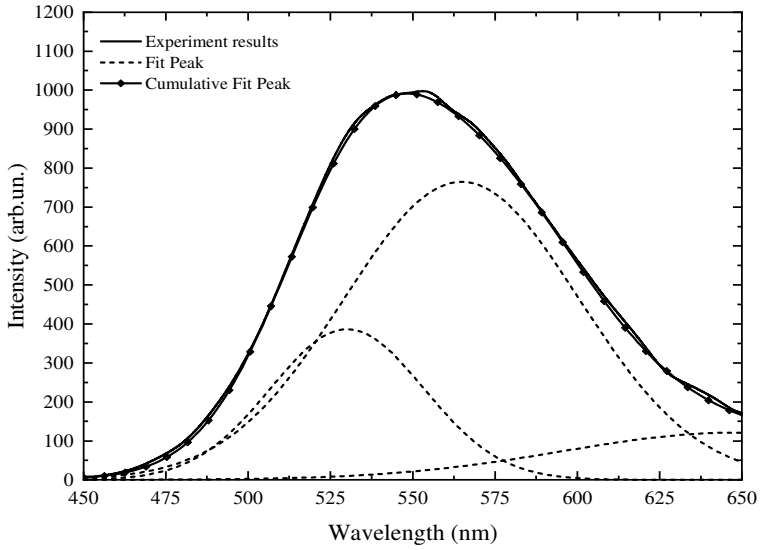
3. Results and discussions

The photoluminescence spectra of crystal $Li_2Ge_7O_{15}$ and its decomposing into elementary components was presented on fig. 2. The luminescence band has an asymmetric spectral profile with a maximum at 548 nm. The best approximation of the observed luminescence band was obtained using three elementary spectral components.

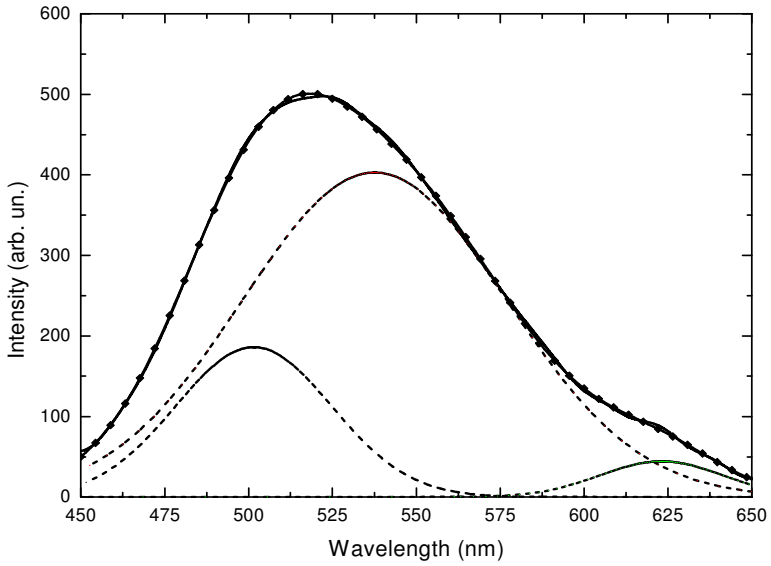
The photoluminescence spectra of crystal $Li_2Ge_7O_{15}$ was presented on fig. 2 (b) when excited by a LED. The spectrum has an asymmetric spectral profile with a maximum at 517 nm, which is shifted by 30 nm to the short-wavelength region of the spectrum compared with another wavelength exciting.

The luminescence spectrum of Li_2O – $7GeO_2$ glass with an admixture of copper (0.67%) and its decomposition into elementary components is shown in Fig. 3. The spectrum has an asymmetric spectral profile with a maximum at 537 nm, which is shifted

by 11 nm to the short-wavelength region of the spectrum compared to a lithium germanate crystal. According to the simulation results, it was found that the spectrum consists of two elementary bands.



(a)



(b)

Fig. 2. The photoluminescence spectrum of crystal $Li_2Ge_7O_{15}$: (a) when excited by a semiconductor laser with λ_{ex}=405 nm; (b) when excited by a LED with λ_{ex}=365 nm

The luminescence spectrum of Li_2O – $7GeO_2$ glass with an admixture of copper (0.67%) and its decomposition into elementary components is shown in Fig. 3. The spectrum has an asymmetric spectral profile with a maximum at 537 nm, which is shifted

by 11 nm to the short-wavelength region of the spectrum compared to a lithium germanate crystal. According to the simulation results, it was found that the spectrum consists of two elementary bands.

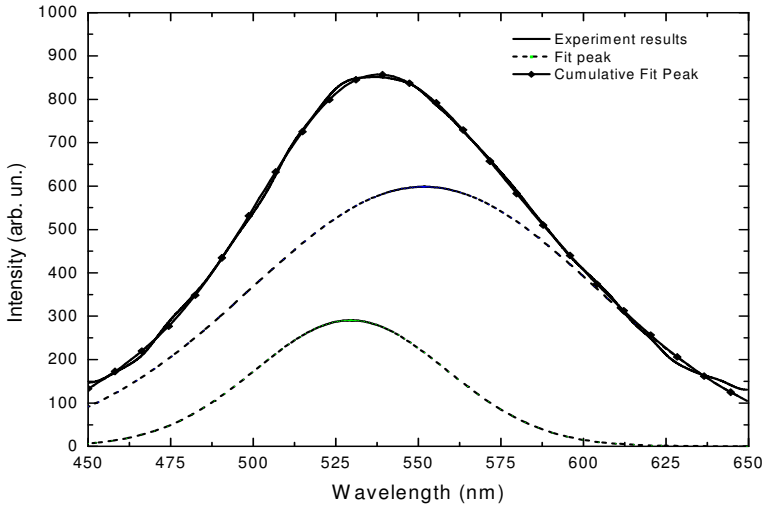


Fig. 3. The photoluminescence spectrum of $Li_2O - 7GeO_2$ glasses doped byCu^{2+} (0,67%)

The photoluminescence spectra of glass $Li_2O - 7GeO_2$ with impurity of chromium ions (0,01%) and its decomposing into elementary components was presented on fig. 4. The spectrum has an asymmetric spectral profile with a maximum at 532 nm, which is shifted by 16 nm to the short-wavelength region of the spectrum compared to a lithium germanate crystal. An increase in the luminescence intensity is observed starting from 600 nm, due to the manifestation of the emission band of chromium ions Cr^{3+}.The spectrum consists of two elementary bands, one of which corresponds to the luminescence of Cr^{3+} ions with a maximum in the long-wavelength region of the spectrum.

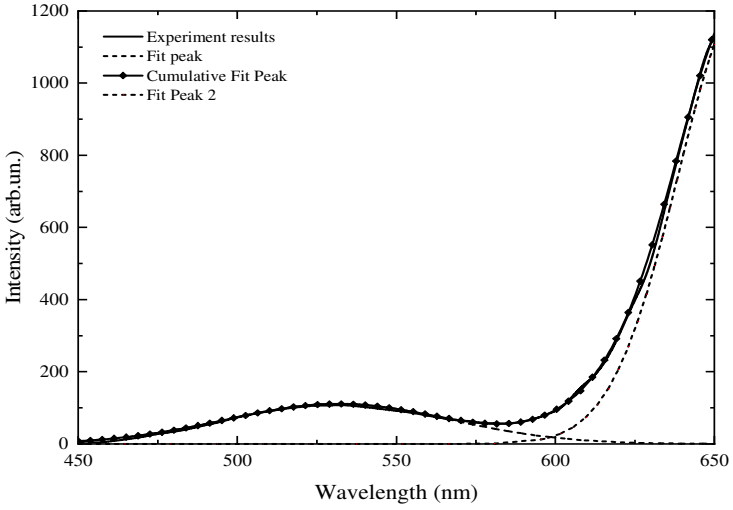


Fig. 4. The photoluminescence spectrum of $Li_2O - 7GeO_2$ glasses doped by Cr^{3+} (0,01%)

The results of the decomposition of the luminescence spectra into spectral components are presented in table 1.

Table 1

The parameters of photoluminescence spectra

Sample	Excitation wavelength	Luminescence band		Spectral components		
		λ_{max}, nm	$\Delta\lambda_{1/2}$, nm	λ_1, nm	λ_2, nm	λ_3, nm
$Li_2Ge_7O_{15}$	λ_{ex}=365 nm	517	95	501	537	623
	λ_{ex}=405 nm	548	97	530	565	648
Li_2O-$7GeO_2$:Cu^{2+}	λ_{ex}=405 nm	537	108	530	552	-
Li_2O-$7GeO_2$:Cr^{3+}		532	89	532	-	-

The position of the maximum of the luminescence band and its half-width in glasses differ from the values for the crystalline phase. This indicates the influence of structural disordering and impurity ions on the luminescence spectrum due to intrinsic centers. It was shown in [8, 9] that Cr^{3+} ions substitute in the LGO lattice for Ge ions in the GeO_6 octahedral coordination. In work [3], the luminescence of chromium ions in lithium germanate glasses containing the nanocrystalline $Li_2Ge_7O_{15}$ phase was studied in detail and the role of the crystalline environment of chromium ions was shown. The fact of the influence of chromium impurity on the luminescence characteristics due to their intrinsic luminescence centers can be explained by the creation of defects of the "substitutional impurity" type in germanium-oxygen complexes. This indicates the connection of the observed luminescence band with the germanium sublattice, in which the germanium complexes are its own luminescence centers. We can assume that the copper impurity also creates defects in the germanium sublattice leading to a change in the luminescence spectrum. The fact of broadening of the luminescence band indicates this. The intensity of the luminescence band which is due to own luminescence centers in chromium-doped glasses decreases in intensity significantly (in 6 times). It is due to the absorption of broadband luminescence by chromium ions. In this case, the germanium oxygen tetrahedra act as a coactivator of the luminescence of chromium ions.

The fact that the excitation wavelength (λ_{ex} = 405 nm or 365 nm were used) affects the characteristics of the intrinsic luminescence spectrum in the $Li_2Ge_7O_{15}$ crystal indicates a complex nature of the energy spectrum of intrinsic luminescence centers.

4. Conclusions

Thus, in the present work, the regularities of the influence of disordering and additionally introduced impurities on the luminescence spectrum of crystals and glasses in the system Li_2O - $7GeO_2$ are revealed.

The results obtained confirm that the main intrinsic luminescence centers are germanium ions in the nearest oxygen environment. For glasses doped with chromium ions, the effect of a sharp decrease in intrinsic luminescence due to the transfer of energy to chromium ions was observed. In this case, germanium-oxygen complexes play the role of a co-activator of luminescence of chromium ions.

The results obtained confirm that the main intrinsic luminescence centers are germanium ions in the nearest oxygen environment.

References

1. **Kukhars′kyy, I.Y.** Vlasni tsentry lyuminestsentsiyi i rekombinatsiyni protsesy v polimorfnykh vydozminakh hermanatu vismutu: avtoreferat dysertatsiyi na zdobuttya naukovoho stupenya kandydata fizyko-matematychnykh nauk / Kukhars′kyy Ihor Yosyfovych // In-t fiz. optyky, L′viv – 2010, – 16 p.

2. **Poperenko, L.V** Osoblyvosti optychnykh vlastyvostey litiy-hermanatnoho skla ta sklokeramiky u vydymiy oblasti spektra / L.V. Poperenko, M.P. Trubitsyn, S.H. Nedil′ko ta in. // Visnyk Kyyivs′koho natsional′noho universytetu imeni Tarasa Shevchenka. Fizyko-matematychna seriya. – 2015. – № 4. – P. 213 – 216.

3. **Vasilevskaya, T.N.** Luminescence of Cr^{3+} impurity ions in $Li_2Ge_7O_{15}$ nanocrystals and clusters embedded in lithium germanate glasses / T.N. Vasilevskaya, A.A. Kaplyanskii, A.B. Kulinkin, S.P. Feofilov // Physics of the Solid State – 2003. – Vol. 45, – No. 5, – P. 961 – 968. Translated from Fizika Tverdogo Tela – P. 915 – 922.

4. **Yegranov, A.V.** Spektroskopiya kislorodnykh i vodorodnykh primesnykh tsentrov v shchelochno–galoidnykh kristallakh / A.V. Yegranov, Ye.A. Radzhabov // Novosibirsk: Nauka. – 1992, – 160 p.

5. **Gorobets, B.S.** Spektry lyuminestsentsii mineralov. Spravochnik / B.S. Gorobets., A. A. Rogozhin // Izd-vo VIMS – 2001. – ISBN: 5-901837-01-0.

6. **Polisadova, Ye.F.** Lyuminestsentsiya kristallov s oksianionami i oksidnykh stekol pri vozbuzhdenii impul'sami potoka elektronov: avtoreferat dissertatsii na soiskaniye uchenoy stepeni doktora fiziko-matematicheskikh nauk / Polisadova Yelena Fedorovna // Natsional'nyy issledovatel'skiy Tomskiy politekhnicheskiy universitet – 2017. – 44 p.

7. **Sigaev, V.N.** Raman and Dielectric Spectra of the Glass and Single Crystal of the Composition $Li_2Ge_7O_{15}$ in the Frequency Range 3–1000 cm^{-1}: II. The Influence of Phase Separation / V.N. Sigaev, S.V. Lotarev, E.N. Smelyanskaya, P.D. Sarkisov, A.A. Volkov, G.A. Komandin, V.V. Koltashev, V.G. Plotnichenko // Glass Physics and Chemistry – 2006, – Vol. 32, No. 5. – P. 497 – 504.

8. **Powell, R.C**. Temperature dependence of the widths and positions of the R lines in $Li_2Ge_7O_{15}:Cr^{3+}$ / Richard C. Powell // J. Appl. Phys. – 1968. – No. 39, P. 4517.

9. **Powell, R.C**. Energy transfer between chromium ions in nonequivalent sites in $Li_2Ge_7O_{15}$ / Richard C. Powell // Phys. Rev. – 1968. – No. 173. – P. 358.