UDC 621.315.592

I. K. DOYCHO[1], S. A. GEVELYUK[1], O. O. PTASHCHENKO[1], E. RYSIAKIEWICZ-PASEK[2], S. O. ZHUKOV[1]

[1]I. I. Mechnikov Odesa National University, Dvoryanska St., 2, Odesa, 65082, Ukraine
[2] Institute of Physics, Wrocław University of Technology, W.Wyspianskiego 27, 50-370 Wrocław, Poland

POROUS GLASSES WITH CDS INCLUSIONS LUMINESCENCE KINETICS PECULIARITIES

The kinetics of the luminescence of porous glasses with CdS inclusions was studied at liquid nitrogen temperature. It is shown that the luminescence decay curves after excitation switch-off are different for different types of glasses. For CdS in matrices with small enough pores, a short-time "flash" of the luminescence was observed after the excitation turn-off. Additional doping of the samples with Na_2S enhanced the "flash". The flash intensity and duration depended on the exciting photons energy. The effect is explained by thermo-optical excitation of electrons.

1. INTRODUCTION

Nanocrystals of semiconductors and, in particular III–V materials, in porous glass are prospective for optical and electronic applications. The complexity of porous glass morphology and a rich luminescent spectrum of bulk CdS [1-4] allows to expect the appearance of various point defects which could be considered as shallow traps and, in other cases, are the centers of luminescence. While studying the luminescence, it is necessary to take into account both the contribution of charge carrier recombination as well as the changes in optical properties of the porous matrix caused by the excitation. Some information about the mechanism of the luminescence excitation, as well as on the nature of radiative recombination, could be obtained by an analysis of the luminescence rise and decay curves [1, 5].

The present paper investigates photo-luminescence stationary and transient characteristics of CdS nano-formations in a porous glass matrix at the temperature of 77 K. A tentative model is used in order to explain some peculiarities of the luminescence decay curves observed.

2. EXPERIMENTAL PROCEDURE

Porous silicate glasses obtained from the two-phase sodium-boron-silica glasses by chemical etching of the unstable sodium-borate phase in hydrochloric acid [6] were used in our experiments as a model matrix medium for forming the semiconductor nano-particles. An initial two-phase glass was annealed at 760 K or 930 K for 100 and 150 hours, respectively, in order to enhance the phase separation. After a subsequent etching of the glass annealed at 760 K, we obtained mesoporous glass with the mean pore radius about 15 nm (glass of A type). A similar treatment of the glass annealed at 930 K gives the mean pore radius of 75 nm (glass of C type).

The etching solution used for etching the sodium-borate phase off, interacted also with the silicate skeleton, which led to the formation of the secondary silica gel inside the pores.

It is possible to remove the secondary silica gel from pores almost completely by the subsequent treatment in KOH solution. However, it leads to an excessive etching of the pores. After such additional treatment of A-glass we obtained a glass with gel-free pores of 23 nm radius. It is referred in this paper as B-glass.

An additional KOH solution etching of C-glass produced gel-free pores with the radius of 160 nm. It is referred as D-glass.

CdS were impregnated into the glasses containing silica gel (A) and also into B- and D-glasses which were practically free of silica gel. CdS nanoclusters in the porous matrices were obtained by chemical deposition using the technique described in [3, 7].

For the increase of the of sulfur ions content (playing the role of a luminescence activator), some of the prepared samples were saturated with Na_2S in water solution [8].

Luminescence was excited by the monochromatized light of a 1 kW Xenon lamp over the wavelength range of 400-700 nm. The luminescence spectra, as well as the excitation spectra, were measured in stationary and transient regimes. Luminescence rise- and decay curves were analyzed. All the measurements were performed at the liquid nitrogen temperature (77 K) using a standard set-up.

Some of specimens were gamma-irradiated using a Co^{60} facility with the power of 9.8 rad/s. This power was used to induce some modification of the material recombination properties [9], called a small dose effect.

3. EXPERIMENTAL RESULTS

Curves 1 and 2 at Fig. 1 present the photoluminescence spectra of CdS clusters in an A-matrix before and after Na_2S saturation, respectively. It is seen that the main red luminescence band is strongly broadened. The short-well shoulder shows that it is not elementary one. Na_2S saturation enhances the luminescence intensity and shifts the spectrum to shorter wavelengths.

Fig. 2 illustrates the luminescence spectrum evolution after switch-off the excitation of A-sample with Na_2S excess. It is seen that the luminescence spectrum changes in time. The phosphorescence band at 725 nm has much higher decay time than the short-wavelength part of the spectrum. It suggests that the photon generation of 725 nm band and the short-wavelength radiative recombination are caused by the differently located centers.

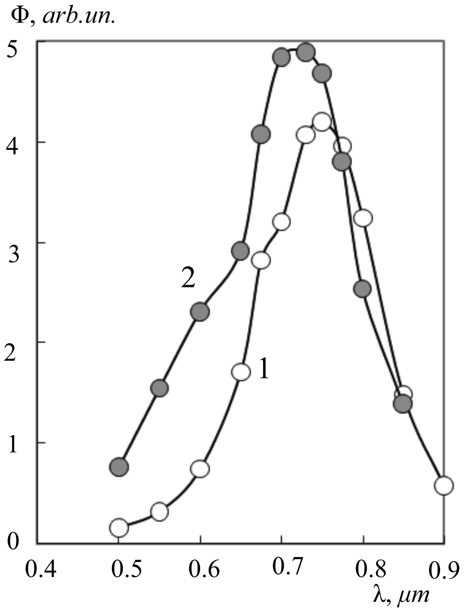

Fig. 1. Photoluminescence spectra of CdS clus-ters in A-matrix: 1 — initial; 2 — after Na_2S saturation

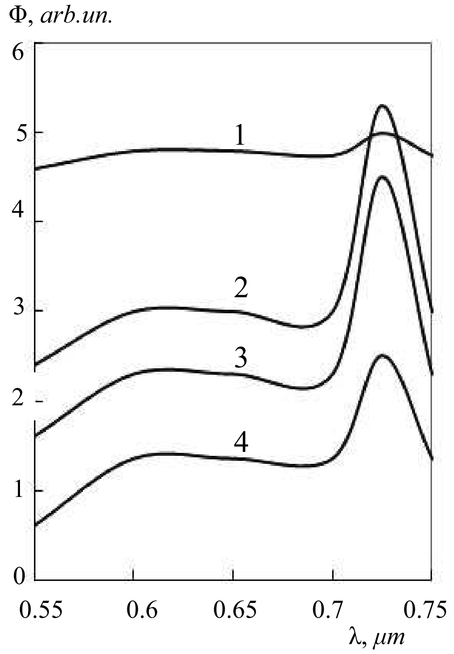

Fig. 2. Phosphorescence spectra of *A*-sample with Na_2S excess at different times after switching off the excitation: 1 — 0.2 s; 2 — 0.8 s; 3 — 1.2 s; 4 — 2.0 s.

Curves 1, 2, and 3 at Fig. 3 show the luminescence rise after switching on the excitation in A-, B-, and D-samples. The rise curves for all of the glass types practically coincide and are exponential:

$$\Phi(t) = \Phi_0[1 - \exp(-t/\tau_r)], \quad (1)$$

where Φ_0 is a constant; τ_r denotes the rise time. For all the curves at Fig. 3 τ_r =1.8 s.

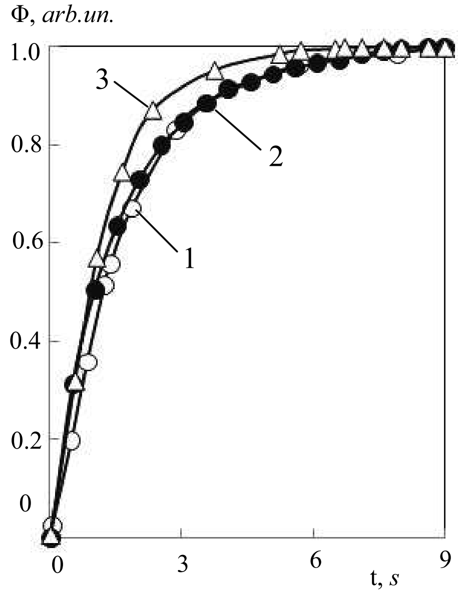

Fig. 3. CdS nanoclusters photoluminescence rise curves for different types of porous glass matrix after 500 nm excitation: 1 — A; 2 — B; 3 — D.

Curve 1 at Fig. 4 represents the phosphorescence decay for CdS in pores of B-glass (in pores with small diameter). The curve has a shoulder at the beginning of the decay. After γ-irradiation with a dose of 10^4 rad, the shoulder disappears (low dose effect), what is illustrated by curve 3, and the decay curve is practically identical to curve 2 (for CdS in wide pores).

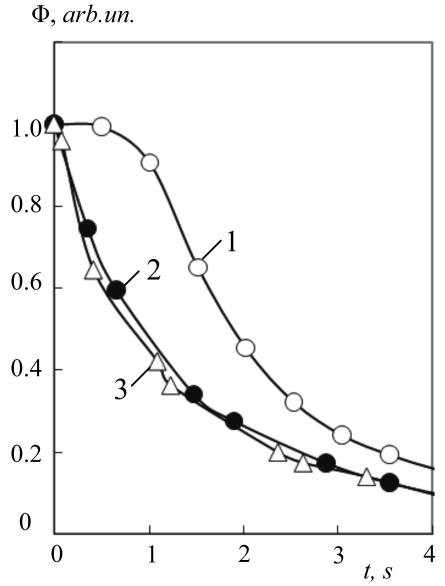

Fig. 4. CdS phosphorescence decay curves in *B*- (1 and 3) and *D*-(2) matrices. 3 – after γ-irradiation with a dose of 10^4 rad.

The decay curve 2 at Fig. 4, measured on CdS in D-matrix, is exponential:

$$\Phi(t) = \Phi_0\exp(-t/\tau_d), \quad (2)$$

where τ_d is the decay time. For curve 2 τ_d=1.78 s. The rise- and decay times are very high:

$$\tau_r, \tau_d >> \tau_n, \quad (3)$$

where τ_n is the life time for electrons (τ_n~1 ms). The strong inequality (3) suggests that CdS microcrystals in pores have very high concentration of shallow traps, which are in equilibrium with c-band.

Our measurements show that the phosphorescence kinetics of CdS clusters in A-glass usually exhibits a flash-up after the excitation turn-off, as demonstrated at Fig 5. Curve 1, measured after excitation with photons of λ = 550 nm (hν = 2.25 eV), has a pronounced shoulder. Excitation at λ = 450 nm (hν = 2.76 eV) leads to a flash, as illustrated with curve 2 at Fig. 5. A treatment of the sample in Na_2S enhances the flash, as shown by curves 3, 4. A comparison of curves 3 and 4 at Fig. 5, obtained after excitation with photons of hν = 2.25 eV and hν = 2.76 eV, correspondingly, demonstrates that the flash becomes more detectable with increasing photon energy.

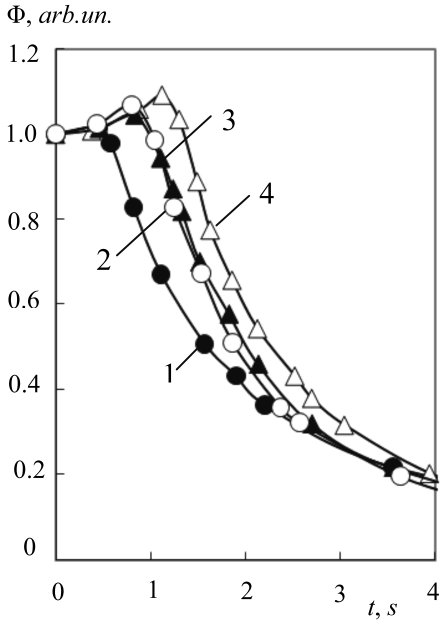

Fig. 5. Decay kinetics of CdS nanoclusters phosphorescence in *A* — matrices: 1, 2 – initial; 3, 4 – after Na_2S-treatment. Curves 1, 3 were measured after excitation with λ=550 nm; 2, 4 – after illumination with λ=450 nm.

The intensity of the flash is different for various phosphorescence spectral bands. The most intensive flash is observed in the band at 725 nm for CdS clusters in A-matrix with the excess of Na_2S after the 450 nm excitation. This band is dominant in the stationary photoluminescence spectrum of these samples, as shown by curve 2 at Fig. 1, and has a higher decay time, as shown at Fig. 2.

4. MODEL AND DISCUSSION

The most interesting result of our experiment is the effect of the mean pore size on the photoluminescence and phosphorescence spectra and the kinetics. We can analyze this effect by the use of a recombination scheme represented at Fig. 6.

The electron-hole pair generation of intensity G is provided by photons absorption. Additional generation G_t has photo-thermal nature. The observed very long rise- and decay times suggest the presence of a high concentration of shallow traps *t*, being in thermal equilibrium with c-band. Radiative recombination occurs at deep *r*-centers. Non-radiative recombination takes place at deep *s*-centers ("fast recombination centers").The corresponding differential equations set is as follows:

$$\frac{dn}{dt} = G + G_t - C_t p_t n + C_t N_{ct} n_t - C_s p_s n - C_r p_r n \; ; \quad (4)$$

$$\frac{dp_r}{dt} = C'_r n_r p - C_r p_r n \; ; \quad (5)$$

$$\frac{dp_s}{dt} = C'_s n_s p - C_s p_s n \; ; \quad (6)$$

$$\frac{dn_t}{dt} = C_t p_t n - C_t N_{ct} \; , \quad (7)$$

where *n*, *p* are the free carriers concentrations; C_t, C_r, C_s denote the electron capture coefficients for *t*-, *r*- and *s*- centers, respectively; C'_r, C'_s are the hole capture coefficients for *r*- and *s*- centers, correspondingly; n_t, n_r, n_s are the concentrations of electrons on *t*-, *r*- and *s*- centers, respectively; p_t, p_r, p_s are the concentrations of empty *t*-, *r*- and *s*- centers, respectively;

$$N_{ct} \equiv N_c \exp(-E_{ct} / kT) \; , \quad (8)$$

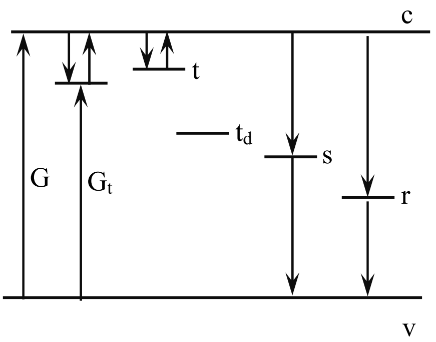

Fig. 6. Recombination scheme for photo-luminescence in CdS clusters

N_c is the effective state density in c-band; E_{ct} is the depth of *t*-level; *kT* is the Boltzmann factor.

The neutrality equation can be written as

$$n + n_t = p_r - p_r^0 + p_s \; , \quad (9)$$

where p_r^0 is determined by the concentration of electrons on deep t_d traps. In (9) the strong inequality

$$n >> p \quad (10)$$

is taken into account as well.

For *s*-centers, as fast non-radiative recombination centers in CdS, the inequalities

$$C_s >> C_r ; \; p_s << p_r \quad (11)$$

are valid.

The luminescence (and phosphorescence) the intensity could be expressed as

$$R_r = C_r p_r n \; . \quad (12)$$

In CdS as a quasi-monopolar semiconductor a strong inequality

$$n >> p \quad (13)$$

takes place.

The observed exponential rise- and decay curves, depicted at Figs.3 and 4, suggest that differential equations (4) — (7) for our case are linearized. It means that in (12)

$$p_r = const\,. \tag{14}$$

And this could occur if we have in the equality (9)

$$p_r \cong p_r^0 >> n + n_\tau, p_s\,. \tag{15}$$

Moreover, it means that the concentration n_t of electrons, captured on shallow *t*-centers, is proportional to free electrons concentration *n*. It could occur in the case of

$$n_t << N_t, \tag{16}$$

where N_t is the concentration of *t*-centers. In this case,

$$n + n_t = Mn\,, \tag{17}$$

where

$$M = 1 + N_t / N_{ct}\,, \tag{18}$$

and $M = const$ at a fixed temperature.

The solution of the equation set (4) — (7) at these assumptions gives for photoluminescence rise and decay curves expressions (1) and (2), respectively, with

$$\tau_r = \tau_d = M\tau_n\,, \tag{19}$$

where τ_n is the electron life time.

As mentioned above, our measurements give $\tau_r \cong \tau_d = 1.8$ s. Taking into account that in CdS $\tau_n \sim 1$ ms, we conclude that the CdS clusters contain high concentration of shallow centers, so that $M \sim 10^3$.

As seen at Figs. 4 and 5, CdS clusters under certain conditions exhibit a phosphorescence flash. The flash-effect could be explained by using the model presented above. The role of photothermal electron generation and presence of two kinds of recombination centers are essential for this explanation. From equation (4), in a stationary case, we obtain for the stationary electron concentration

$$n^{st} = (G + G_t)/(C_r p_r^0 + C_s p_s^{st}) \tag{20}$$

and for the radiative recombination intensity

$$R_r^{st} = g_r (G + G_t)\,, \tag{21}$$

where

$$g_r \equiv C_r p_r^0 /(C_r p_r^0 + C_s p_s^{st})\,. \tag{22}$$

After turn off excitation *G* the intensity of the photothermal excitation

$$G_t \neq 0\,, \tag{23}$$

because the concentration of electrons on the corresponding centers exceeds its equilibrium value. Moreover, the fast recombination centers (s-centers) for a short time are filled by electrons, so

$$P_s \to 0\,, \tag{24}$$

and one could obtain for the electrons concentration

$$n = G_t /(C_r p_r^0) \tag{25}$$

and for the radiative recombination intensity

$$R_r = G_t\,. \tag{26}$$

The intensity of the photothermal excitation G_t decreases with time, and the phosphorescence intensity falls down as well.

A comparison of (21) and (26) gives the condition for appearance of the phosphorescence flash:

$$G_t > g_r /(1 - g_r) G\,. \tag{27}$$

Our measurements reveal the following conditions for the flash-effect in CdS nanocrystals: a) the pores in the matrix must be small enough. The effect occurs only in *A*- and *B*-matrices; b) the flash is observed only in 725 nm phosphorescence band; c) Na_2S treatment enhances the effect; d) excitation with photons of hν = 2.75 eV gives more pronounced effect than of 2.25eV; e) γ-irradiation suppresses the effect.

The first condition suggests that the flash-effect is characteristic for small enough CdS nanocrystals. This observation is in agreement with results [5] and the fact that lowering the nanocrystals' size makes slower the CdS phosphorescence decay [3, 4, 7].

The influence of Na_2S treatment on the flash intensity argues that point defects, containing sulfur atoms, are responsible for this effect. Inhibition of the effect by γ-radiation can be explained by destroying the low-size nanoclusters as a result of γ-quanta absorption [9]. The photoluminescence and phosphorescence of CdS in *D*-glasses is less sensitive to radiation, which is in accordance with previously reported results [9]. The flash-effect disappeared after a long time storage (over half a year; *A*-specimens were exposed to the air). It is also suppressed by low temperature annealing of the samples in air. This phenomenon could be attributed to slow oxidation of excess sulfur during the storage in the open air.

5. CONCLUSIONS

1. The phosphorescence of CdS nanoclusters in porous glass exhibits a flash after excitation turn-off. This effect occurs only in glass with sufficiently small pores and can be ascribed to recombination in small enough CdS clusters. The flash is observed only in the spectral band of hν = 1.71 eV which corresponds to the recombination of free electrons at deep centers.
2. The recombination model, that includes two kinds of recombination centers and centers responsible for the photo-thermal electron generation, could explain the flash-effect.
3. The introduction of the excess sulphur ions enhances the effect. It suggests that the centers, responsible for flash, contain sulphur atoms.
4. The flash-effect is suppressed by γ-irradiation as well as by low-temperature annealing in air. This instability could be ascribed to small CdS clusters destruction. The γ-stability of CdS nanoclusters is enhanced with the increase of their size.

References

1. Guyot-Sionnest P., Halas N.J., Mattoussi H., Wang Z.L., Woggon U. Quantum Confined Semiconductor Nanostruc-

tures // *MRS Symposium Proceedings*. — 2004. — V. 789. 429 p.
2. Smyntyna V.A., Skobeeva V.M., Malushin N.V., Pomogailo A.D. Influence of matrix on photoluminesence of CdS nanocrystals // *Photoelectronics*. — 2006. — V. 15. P. 38-42.
3. Gevelyuk S.A., Doycho I.K., Mak V.T., Zhukov S.A. Photoluminescence and structural properties of nano-size CdS inclusions in porous glasses // *Photoelectronics* — 2007. — V. 16. P. 75-79.
4. Rysiakiewicz-Pasek E., Polańska J., Gevelyuk S.A., Doycho I.K., Mak V.T., Zhukov S.A. The photoluminescent properties of CdS clusters of different size in porous glasses // *Optica Applicata*. — 2008. — V. 38, № 1. P. 93-100.
5. Gaponenko S.V. *Optical Properties of Semiconductor Nanocrystals* // Cambridge University Press: 1998. — 300 p.
6. Rysiakiewicz-Pasek E., Gevelyuk S.A., Doycho I.K., Vorobjova V.A. Application of Porous Glass in Ophtalmic Prosthetic Repair // *Journal of Porous Materials*. — 2004. — V. 11, № 1. P. 21-29.
7. Rysiakiewicz-Pasek E., Zalewska M., Polańska J. Optical Properties of CdS-doped Porous Glasses // *Optical Materials*. — 2008. — V. 30, № 5. P. 777-779.
8. Fu Z., Zhou S., Shi J., Zhang S. Effects of Precursors on the Crystal Structure and Photoluminescence of CdS Nanocrystalline// ***Material Research Bulletin***. — 2005. — V. 40. P. 1591-1598.
9. Doycho I.K., Gevelyuk S.A., Kovalenko M.P., Prokopovich L.P., Rysiakiewicz-Pasek E. Small doses γ-irradiation effect on the photoluminescence properties of porous glasses // *Optica Applicata*. — 2003. — V. 33, № 1. P. 55-60.

UDC 621.315.592

I. K. Doycho, S. A. Gevelyuk, O. O. Ptashchenko, E. Rysiakiewicz-Pasek, S. O. Zhukov

POROUS GLASSES WITH CDS INCLUSIONS LUMINESCENCE KINETICS PECULIARITIES

Abstract

The kinetics of the luminescence of porous glass with CdS inclusions was studied at liquid nitrogen temperature. It is shown that the luminescence decay curves after excitation switching-off are different for different types of glasses. For CdS in matrices with small enough pores, a short-time “flash” of the luminescence was observed after the excitation turn off. Additional doping of the samples with Na_2S enhanced the “flash”. The flash intensity and duration depended on the exciting photons energy. The effect is interpreted by thermo-optical excitation of electrons.

Key words: doped porous glasses, cadmium sulphide, luminescence kinetics.

УДК 621.315.592

И. К. Дойчо, С. А. Гевелюк, А. А. Птащенко, Е. Рысакевич-Пасек, С. А. Жуков

ОСОБЕННОСТИ КИНЕТИКИ ЛЮМИНЕСЦЕНЦИИ ПОРИСТОГО СТЕКЛА С ВКЛЮЧЕНИЯМИ CDS

Резюме

Исследована кинетика фотолюминесценции пористого стекла с включениями CdS при температуре жидкого азота. Показано, что кривые спада фотолюминесценции после выключения возбуждения различны для различных типов стёкол. Для CdS в матрицах с достаточно малыми порами наблюдалась кратковременная вспышка люминесценции после выключения возбуждения. Дополнительное насыщение образцов Na_2S усиливало указанную вспышку. Интенсивность и длительность вспышки зависела от энергии возбуждающих фотонов. Эффект объяснён термооптическим возбуждением электронов.

Ключевые слова: кинетика люминесценции, пористое стекло, сульфид кадмия.

УДК 621.315.592

І. К. Дойчо, С. А. Гевелюк, О. О. Птащенко, Е. Ришякевич-Пасек, С. О. Жуков

ОСОБЛИВОСТІ КІНЕТИКИ ЛЮМІНЕСЦЕНЦІЇ ШПАРИСТОГО СКЛА З ВКРАПЛЕННЯМИ CDS

Резюме

Досліджено кінетику люмінесценції шпаристого скла із вкрапленнями CdS при температурі рідкого азоту. Продемонстровано, що криві спаду люмінесценції після вимкнення збудження неоднакові для різних типів скла. Для CdS в матрицях з достатньо малими порами спостерігався короткочасний спалах люмінесценції після вимкнення збудження. Додаткове насичення зразків Na_2S підсилювало зазначений спалах. Інтенсивність і тривалість спалаху залежала від енергії збуджуючих фотонів. Ефект пояснено термооптичним збудженням електронів.

Ключові слова: кінетика люмінесцеції, шпаристе скло, сульфід кадмію.