

Yu. A. Nitsuk, Yu. F. Vaksman, I. V. Tepliakova, A. A. Rimashevskiy

I. I. Mechnikov Odesa National University
e-mail: nitsuk@onu.edu.ua

SYNTHESIS AND LUMINESCENCE PROPERTIES OF ZnSe:Al NANOPARTICLES

Colloidal nanocrystals of ZnSe:Al were synthesized in organic polymer matrices. The optical absorption and long-wavelength luminescence were studied, the average sizes of nanoparticles were determined, the efficiency of the transition from bulk crystals to nanocrystals was shown, and the types of optical transitions were determined.

Introduction

Semiconductor colloidal nanocrystals of the A_2B_6 group are promising materials for biomedical marking and visualization. The most widely represented in the studies are CdS and CdSe nanocrystals [1,2], which have tunable, wide and intense emission bands. However, many results show that any leakage of cadmium from nanocrystals will be toxic and fatal to biological systems. In connection with this, the synthesis of nanomaterials, not cadmium entities, is topical. Such materials include zinc chalcogenides, and zinc selenide in particular.

Being a wide-band semiconductor, ZnSe is ideally suited for the creation on its basis of optoelectronics devices and biomedical imaging. Doping ZnSe allows the realization of luminescent radiation in the visible and near infrared wavelengths. At present, ZnSe nanocrystals doped with transition elements such as Cu, Mn, Co have been successfully synthesized [3]. At the same time, there is no information on the preparation of zinc selenide nanoparticles doped with Group III donor elements (Al, Ga, In). Investigations of the photoluminescence of bulk ZnSe:Al crystals showed that in zinc selenide an Al impurity is the best activator in the visible range [4]. So the preparation and investigation of the luminescent properties of ZnSe:Al nanocrystals is relevant.

The purpose of this work is the development of an ecological approach to the synthesis of ZnSe:Al nanocrystals, the study of their luminescent properties and the establishment of natural emission transitions in these nanocrystals.

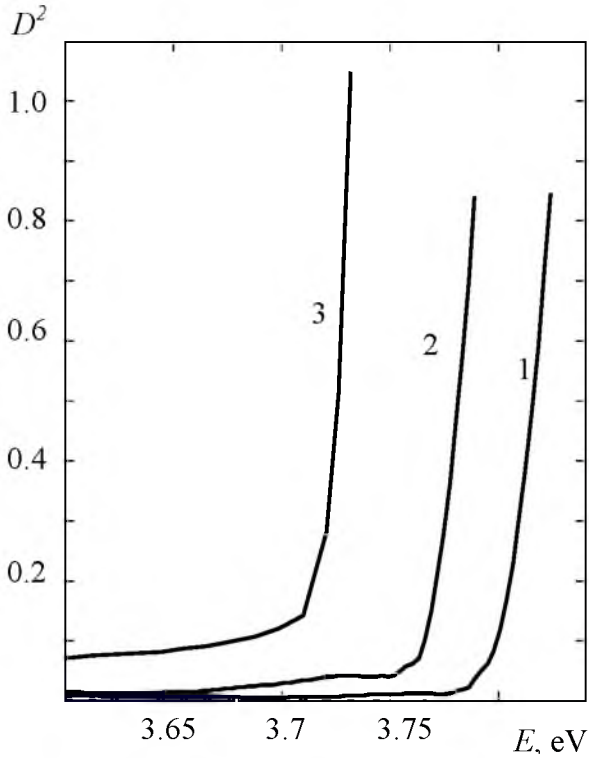
Experimental

The study used commercial reagents Beijing Reagent Company. $ZnCl_2$ was the source of zinc ions. The source of Se^{2-} ions was sodium selenosulfate Na_2SeSO_3 , which was prepared with an aqueous Na_2SO_3 solution and powdered Se (99%). Polyvinyl alcohol, gelatin or lactose was used as the growth stabilizer of nanoparticles. The doping with Al ions was carried out by the addition of Al_2Cl_3 . The resulting colloidal solution containing ZnSe and ZnSe:Al nanoparticles was deposited on quartz substrates, then the solvent evaporated, forming membranes for measuring optical absorption and photoluminescence.

The optical absorption and photoluminescence spectra were recorded with an MDR-6 monochromator with a $2400 \text{ groove} \cdot \text{mm}^{-1}$ diffraction gratings in the ultraviolet and $1200 \text{ groove} \cdot \text{mm}^{-1}$ in the visible range.

Investigation of the optical absorption

The optical density spectra of ZnSe and ZnSe:Al nanocrystals were studied. It is established that in all the samples studied the absorption edge is shifted to the region of high energies in comparison with the absorption edge of single crystals of ZnSe, which indicates the presence of quantum size effects in the samples. The influence of the ratio of the concentrations of zinc and selenium sources on the position of the absorption edge was established. The maximum displacement was observed at a ratio of $ZnCl_2$ to Na_2SeSO_3 of 10:1.



The mean radius of the ZnSe, ZnSe:Al particles was estimated from the change in the band gap (ΔE_g) relative to the bulk crystal, using the effective-mass approximation using the equation [5]

$$R = \frac{h}{\sqrt{8 \Delta E_g}} \quad (1)$$

There h is the Planck constant; $\mu = ((m_e^*)^{-1} + (m_h^*)^{-1})^{-1}$, where $m_e^* = 0.17m_e$, $m_h^* = 0.6m_e$ are, respectively, the effective masses of the electron and hole in zinc selenide, m_e is the mass of the free electron; ΔE_g is the difference between the width of the band gap in the nanoparticle and the bulk crystal of ZnSe (2.68 eV). The results of calculations showed that the minimum ZnSe nanoparticles size (3.5 nm) is reached just at the ratio of ZnCl₂ to Na₂SeSO₃ 10: 1 (Fig. 1, curve 1).

Doping of ZnSe nanocrystals with aluminum leads to a shift in the absorption edge to the region of lower energies. The magnitude of the displacement increased with increasing concentration of the aluminum source (Fig. 1, curves 2,3). A similar dependence of the width of the forbidden band on the concentration of the dopant was observed earlier in bulk ZnSe crystals containing the donor impurity In, the impurity ions of the transition el-

ements, and was explained by the presence of an impurity Coulomb interaction [6]. Using relation

$$\Delta E_g = 2 \cdot 10^5 \left(\frac{3}{\pi} \right)^{1/3} \frac{eN^{1/3}}{4\pi\epsilon_0\epsilon_s}, \quad (2)$$

where: e – electron charge, N – concentration of impurities in cm⁻³, $\epsilon_s = 8.66$ is zinc selenide static dielectric constant, the concentration of aluminum impurity in the investigated nanocrystals is determined. 5% solution of Al₂Cl₃ corresponds to the concentration of aluminum in nanocrystals of 10¹⁸ cm⁻³, and 10% solution of Al₂Cl₃ is a concentration of 10¹⁹ cm⁻³.

Investigation of long-wavelength photoluminescence

Investigation of ZnSe nanocrystals photoluminescence spectra is showed the presence of broad photoluminescence bands localized in the 550-850 nm region. The change in the temperature of nanocrystals from 300 to 430 K did not cause a shift in the spectra studied. The position of the spectra remained unchanged even with a change in the width of the forbidden band of nanocrystals. The presence of a number of bend and a large (~ 150 nm) half-width of the bands indicate their non-elementary nature. The decomposition into elementary Gaussian components in the Origin-Pro 7 program revealed a series of elementary emission lines localized at 580, 600, 630, 680, 700, 750 and 800 nm (Fig. 2, a). The identical elementary emission lines were observed earlier in bulk ZnSe single crystals (Fig. 2, b) [4].

Emission at a wavelength of 580 nm appears due to associative native defects ($V_{Zn}V_{Se}$). The emission line at a wavelength of 600 nm appears due to associative defects ($V_{Zn}D_{Se}$) where the donor is either V_{Se} or an uncontrolled donor impurity, an IIV group element, for example, Cl, Br, I. The other emission lines were associated with defects ($V_{Zn}D_{Zn}$) with different distances between donors and acceptors. Here the donor, according to [4], is the uncontrolled impurities Al, In, Ga.

Doping with aluminum during the growth of nanocrystals leads to an increase in the emission intensity in the 500-1000 nm region. Further increase of the emission intensity with increasing

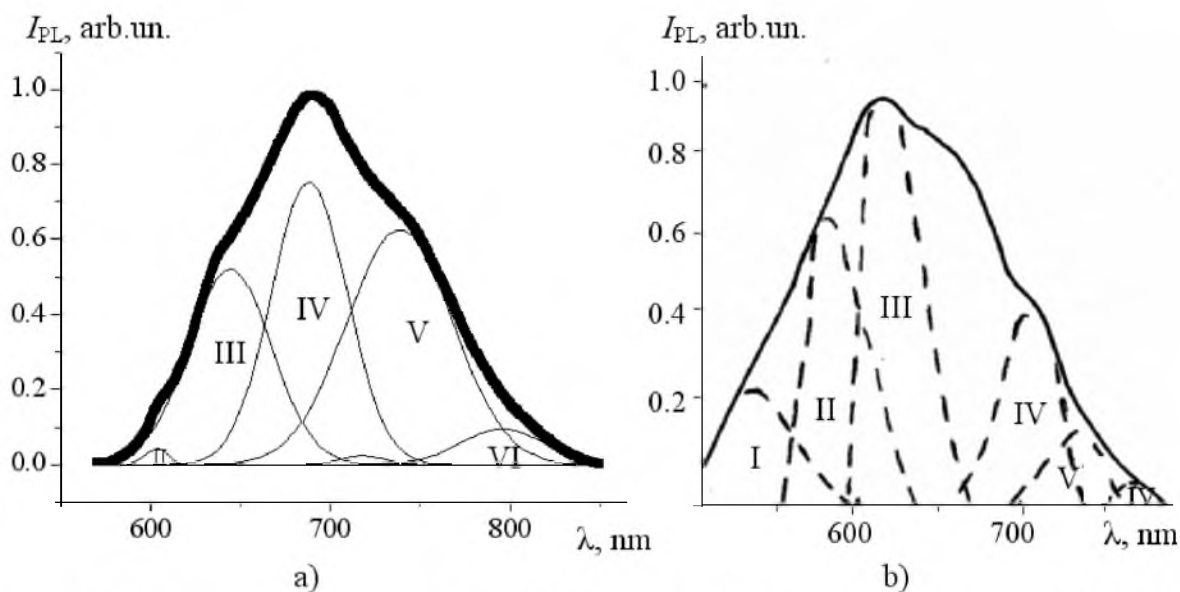


Fig 2. Photoluminescence spectra of (1) ZnSe nanocrystals and (b) ZnSe bulk crystals [4].

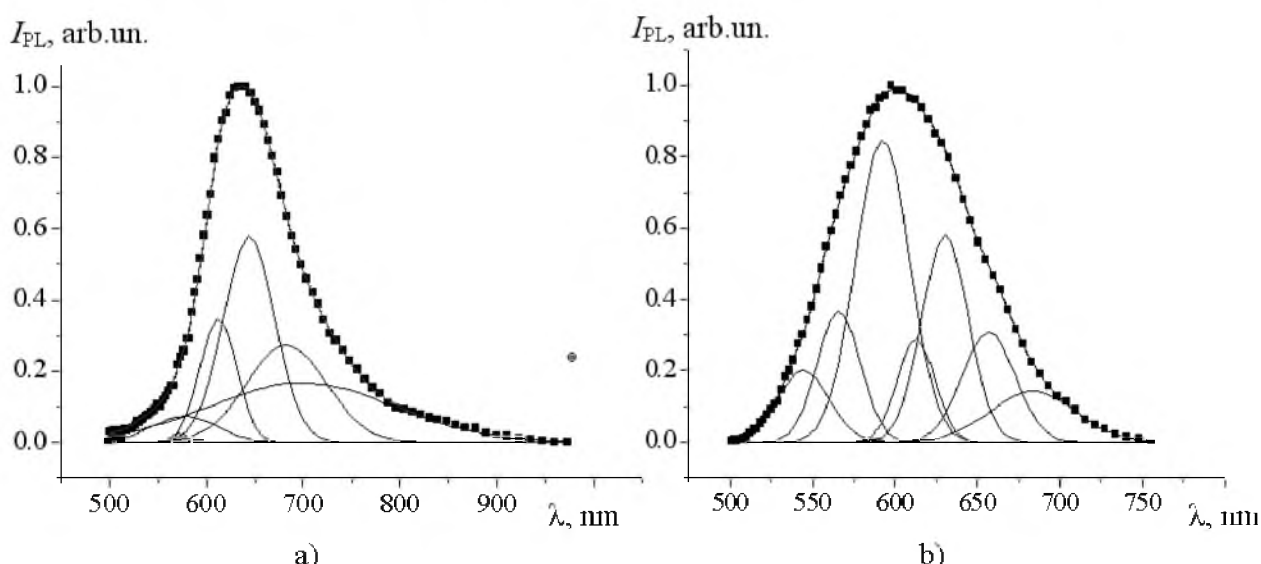


Fig 3. Photoluminescence spectra of (a) ZnSe:Al nanocrystals and (b) ZnSe:Al bulk crystals.

Al_2Cl_3 concentration is explained by an increase of the donor impurity concentration in investigated nanocrystals.

In the emission spectra of ZnSe:Al nanocrystals, elementary emission lines are emitted at 580, 600, 630, 680, and 700 nm. The same emission lines were detected in bulk crystals of ZnSe:Al (Fig. 3, b).

It is established that a change of Al_2Cl_3 concentration, the choice of the stabilizing matrix type does not lead to a shift of the elementary and integral emission lines to the short-wave or long-wave region. The change in technological

conditions leads to a change in the intensity of the elementary emission lines, which is explained by the redistribution of the concentration of native and impurity defects that make up the associative centers. The shift of the emission integrated maximum to the smaller wavelengths region with increasing Al_2Cl_3 concentration from 2 to 10% can be explained by increasing in the intensity of the elementary emission line at 600 nm due to associative defects $(V_{\text{Zn}}\text{Cl}_{\text{Se}})^{\cdot}$.

Conclusions

ZnSe and ZnSe:Al nanoparticles up to 3.5 nm in diameter were successfully synthesized using the “green” synthesis method and organic stabilizing agents. It is shown that ZnSe:Al nanoparticles possess effective long-wave emission and can be used as fluorescent labels. The nature of the radiative transitions in ZnSe and ZnSe:Al nanocrystals is established. It has been experimentally confirmed that when the transition from bulk crystals to nanocrystals does not occur, the emission lines shift toward donor-acceptor pairs.

References

1. X. Peng, M. C. Schlamp, A. V. Kadavanich, and A. P. Alivisatos, “Epitaxial growth of highly luminescent CdSe/CdS core/shell nanocrystals with photostability and electronic accessibility,” *Journal of the American Chemical Society*, vol. 119, no. 30, pp. 7019-7029, 1997.
2. B. O. Dabbousi, J. Rodriguez-Viejo, F. V. Mikulec et al., “(CdSe)ZnS core-shell quantum dots: synthesis and characterization of a size series of highly luminescent nanocrystallites,” *Journal of Physical Chemistry B*, vol. 101, no. 46, pp. 9463–9475, 1997.
3. D. Han, C. Song X. Li. Synthesis and Fluorescence Property of Mn-Doped ZnSe Nanowires // *J. Nanomaterials*. – 2010. - P.1-4.
4. Serdyuk V.V., Korneva N.N., Vaksman Yu.F. Studies of Long-Wave Luminescence of Zinc Selenide Monocrystals // *Phys. Stat. Sol.(a)*. – 1905. – V.91. – P. 173-183.
5. Гусев А.И., Ремпель А.А. Нанокристаллические материалы. – М:Физматлит. – 2000. –С 224.
6. Vaksman Yu.F., Nitsuk Yu.A., Purto Yu.N. and Shapkin P.V. Native and Impurity Defects in ZnSe:In Single Crystals Prepared by Free Growth// *Semiconductors*. – 2001. – V. 35, № 8. – P. 920-926.

This article has been received in May 2017

UDC 621.315.592

Yu. A. Nitsuk, Yu. F. Vaksman, I. V. Tepliakova, A. A. Rimashevskiy

SYNTHESIS AND LUMINESCENCE PROPERTIES OF ZnSe:Al NANOPARTICLES

Summary

Colloidal nanocrystals of ZnSe:Al were synthesized in organic polymer matrices. The optical absorption and long-wavelength luminescence were studied, the average sizes of nanoparticles were determined, the efficiency of the transition from bulk crystals to nanocrystals was shown, and the types of optical transitions were determined.

Key words: ZnSe, ZnSe:Al, nanoparticles, colloidal synthesis, optical properties, luminescence, biomedical markers.

УДК 621.315.592

Ю. А. Ницук, Ю. Ф. Ваксман, І. В. Теплякова, О. А. Рімашевський

СИНТЕЗ ТА ЛЮМІНЕСЦЕНТНІ ВЛАСТНВОСТІ НАНОКРНСТАЛІВ ZnSe:Al

Анотація

Колоїдні наночастинки ZnSe:Al були синтезовані в органічній полімерній матриці. Були досліджені оптичне поглинання та довгохвильова фотолюмінесценція. За зсувом ширини забороненої зони визначений середній розмір наночастинок. Визначена природа випромінювальних переходів.

Ключові слова: ZnSe, ZnSe:Al, наночастинки, колоїдний синтез, оптичні властивості, люмінесценція, біомаркери.

УДК 621.315.592

Ю. А. Ницук, Ю. Ф. Ваксман, И. В. Теплякова, А. А. Римашевский

СИНТЕЗ И ЛЮМИНЕСЦЕНТНЫЕ СВОЙСТВА НАНОКРНСТАЛЛОВ ZnSe:Al

Аннотация

Коллоидные наночастицы ZnSe:Al были синтезированы в органической полимерной матрице. Были исследованы оптическое поглощение и длинноволновая люминесценция. По смещению ширины запрещенной зоны определялся средний размер наночастиц. Определена природа излучательных переходов.

Ключевые слова: ZnSe, ZnSe:Al, наночастицы, коллоидный синтез, оптические свойства, люминесценция, биомаркеры.