

ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)

ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ

Д.В.Сокольский атындағы «Жанармай,
катализ және электрохимия институты» АҚ

Х А Б А Р Л А Р Ы

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
электрохимии им. Д.В. Сокольского»

NEWS

OF THE ACADEMY OF SCIENCES
OF THE REPUBLIC OF KAZAKHSTAN
JSC «D.V. Sokolsky institute of fuel, catalysis
and electrochemistry»

SERIES
CHEMISTRY AND TECHNOLOGY

1 (439)

JANUARY – FEBRUARY 2020

PUBLISHED SINCE JANUARY 1947

PUBLISHED 6 TIMES A YEAR

ALMATY, NAS RK

NAS RK is pleased to announce that News of NAS RK. Series of chemistry and technologies scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of chemistry and technologies in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of chemical sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Web of Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

Б а с р е д а к т о р ы

х.ғ.д., проф., ҚР ҰҒА академигі

М.Ж. Жұрынов

Р е д а к ц и я а л қ а с ы:

Ағабеков В.Е. проф., академик (Белорус)
Волков С.В. проф., академик (Украина)
Воротынцев М.А. проф., академик (Ресей)
Газалиев А.М. проф., академик (Қазақстан)
Ергожин Е.Е. проф., академик (Қазақстан)
Жармағамбетова А.К. проф. (Қазақстан), бас ред. орынбасары
Жоробекова Ш.Ж. проф., академик (Қырғыстан)
Иткулова Ш.С. проф. (Қазақстан)
Манташян А.А. проф., академик (Армения)
Пралиев К.Д. проф., академик (Қазақстан)
Баешов А.Б. проф., академик (Қазақстан)
Бүркітбаев М.М. проф., академик (Қазақстан)
Джусипбеков У.Ж. проф. корр.-мүшесі (Қазақстан)
Молдахметов М.З. проф., академик (Қазақстан)
Мансуров З.А. проф. (Қазақстан)
Наурызбаев М.К. проф. (Қазақстан)
Рудик В. проф., академик (Молдова)
Рахимов К.Д. проф. академик (Қазақстан)
Стрельцов Е. проф. (Белорус)
Тәшімов Л.Т. проф., академик (Қазақстан)
Тодераш И. проф., академик (Молдова)
Халиков Д.Х. проф., академик (Тәжікстан)
Фарзалиев В. проф., академик (Әзірбайжан)

«ҚР ҰҒА Хабарлары. Химия және технология сериясы».

[ISSN 2518-1491 \(Online\)](#)

[ISSN 2224-5286 \(Print\)](#)

Меншіктенуші: «Қазақстан Республикасының Ұлттық ғылым академиясы» Республикалық қоғамдық бірлестігі (Алматы қ.)

Қазақстан республикасының Мәдениет пен ақпарат министрлігінің Ақпарат және мұрағат комитетінде 30.04.2010 ж. берілген №1089-Ж мерзімдік басылым тіркеуіне қойылу туралы куәлік

Мерзімділігі: жылына 6 рет.

Тиражы: 300 дана.

Редакцияның мекенжайы: 050010, Алматы қ., Шевченко көш., 28; 219, 220 бөл.; тел.: 272-13-19; 272-13-18,
<http://chemistry-technology.kz/index.php/en/arhiv>

© Қазақстан Республикасының Ұлттық ғылым академиясы, 2020

Типографияның мекенжайы: «NurNaz GRACE», Алматы қ., Рысқұлов көш., 103.

Главный редактор

д.х.н., проф., академик НАН РК

М. Ж. Журинов

Редакционная коллегия:

Агабеков В.Е. проф., академик (Беларусь)
Волков С.В. проф., академик (Украина)
Воротынцев М.А. проф., академик (Россия)
Газалиев А.М. проф., академик (Казахстан)
Ергожин Е.Е. проф., академик (Казахстан)
Жармагамбетова А.К. проф. (Казахстан), зам. гл. ред.
Жоробекова Ш.Ж. проф., академик (Кыргызстан)
Иткулова Ш.С. проф. (Казахстан)
Манташян А.А. проф., академик (Армения)
Пралиев К.Д. проф., академик (Казахстан)
Баешов А.Б. проф., академик (Казахстан)
Буркитбаев М.М. проф., академик (Казахстан)
Джусипбеков У.Ж. проф. чл.-корр. (Казахстан)
Мулдахметов М.З. проф., академик (Казахстан)
Мансуров З.А. проф. (Казахстан)
Наурызбаев М.К. проф. (Казахстан)
Рудик В. проф., академик (Молдова)
Рахимов К.Д. проф. академик (Казахстан)
Стрельцов Е. проф. (Беларусь)
Ташимов Л.Т. проф., академик (Казахстан)
Тодераш И. проф., академик (Молдова)
Халиков Д.Х. проф., академик (Таджикистан)
Фарзалиев В. проф., академик (Азербайджан)

«Известия НАН РК. Серия химии и технологии».

[ISSN 2518-1491 \(Online\)](#)

[ISSN 2224-5286 \(Print\)](#)

Собственник: Республиканское общественное объединение «Национальная академия наук Республики Казахстан» (г. Алматы)

Свидетельство о постановке на учет периодического печатного издания в Комитете информации и архивов Министерства культуры и информации Республики Казахстан №10893-Ж, выданное 30.04.2010 г.

Периодичность: 6 раз в год

Тираж: 300 экземпляров

Адрес редакции: 050010, г. Алматы, ул. Шевченко, 28; ком. 219, 220; тел. 272-13-19; 272-13-18,

<http://chemistry-technology.kz/index.php/en/arhiv>

© Национальная академия наук Республики Казахстан, 2020

Адрес редакции: 050100, г. Алматы, ул. Кунаева, 142,
Институт органического катализа и электрохимии им. Д. В. Сокольского,
каб. 310, тел. 291-62-80, факс 291-57-22, e-mail:orgcat@nursat.kz

Адрес типографии: «NurNaz GRACE», г. Алматы, ул. Рыскулова, 103.

E d i t o r i n c h i e f

doctor of chemistry, professor, academician of NAS RK
M.Zh. Zhurinov

E d i t o r i a l b o a r d:

Agabekov V.Ye. prof., academician (Belarus)
Volkov S.V. prof., academician (Ukraine)
Vorotyntsev M.A. prof., academician (Russia)
Gazaliyev A.M. prof., academician (Kazakhstan)
Yergozhin Ye.Ye. prof., academician (Kazakhstan)
Zharmagambetova A.K. prof. (Kazakhstan), deputy editor in chief
Zhorobekova Sh.Zh. prof., academician (Kyrgyzstan)
Itkulova Sh.S. prof. (Kazakhstan)
Mantashyan A.A. prof., academician (Armenia)
Praliyev K.D. prof., academician (Kazakhstan)
Bayeshov A.B. prof., academician (Kazakhstan)
Burkitbayev M.M. prof., academician (Kazakhstan)
Dzhusipbekov U.Zh. prof., corr. member (Kazakhstan)
Muldakhmetov M.Z. prof., academician (Kazakhstan)
Mansurov Z.A. prof. (Kazakhstan)
Nauryzbayev M.K. prof. (Kazakhstan)
Rudik V. prof., academician (Moldova)
Rakhimov K.D. prof., academician (Kazakhstan)
Streltsov Ye. prof. (Belarus)
Tashimov L.T. prof., academician (Kazakhstan)
Toderash I. prof., academician (Moldova)
Khalikov D.Kh. prof., academician (Tadjikistan)
Farzaliyev V. prof., academician (Azerbaijan)

News of the National Academy of Sciences of the Republic of Kazakhstan. Series of chemistry and technology.
[ISSN 2518-1491 \(Online\)](#)

[ISSN 2224-5286 \(Print\)](#)

Owner: RPA "National Academy of Sciences of the Republic of Kazakhstan" (Almaty)

The certificate of registration of a periodic printed publication in the Committee of Information and Archives of the Ministry of Culture and Information of the Republic of Kazakhstan N 10893-Ж, issued 30.04.2010

Periodicity: 6 times a year

Circulation: 300 copies

Editorial address: 28, Shevchenko str., of. 219, 220, Almaty, 050010, tel. 272-13-19; 272-13-18,
<http://chemistry-technology.kz/index.php/en/arhiv>

© National Academy of Sciences of the Republic of Kazakhstan, 2020

Editorial address: Institute of Organic Catalysis and Electrochemistry named after D. V. Sokolsky
142, Kunayev str., of. 310, Almaty, 050100, tel. 291-62-80, fax 291-57-22,
e-mail: orgcat@nursat.kz

Address of printing house: «NurNaz GRACE», 103, Ryskulov str, Almaty.

NEWS

OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY

ISSN 2224-5286

<https://doi.org/10.32014/2020.2518-1491.7>

Volume 1, Number 439 (2020), 55 – 63

UDC: 549.331

MRNTI 31.17.29

M.A. Daurenbek¹, A.K. Mazhibaev², A.A. Bakibaev³¹Taraz State University named after M.Kh. Dulati, Taraz, Kazakhstan;²Taraz State Pedagogical University, Taraz, Kazakhstan;³National Research Tomsk State University, Tomsk, Tomsk Region, Russiamdaurenbek@mail.ru 707olo@mail.ru bakibaev@mail.ru**ABOUT MODERN RESEARCH IN THE FIELD
OF COMPLEX SULFIDE COMPOUNDS (STATE AND TRENDS)**

Abstract. The article provides an overview of the most significant scientific papers (from more than 600 literature sources), devoted to the studies of complex sulfides, some of which are given in this research. There are examples of research in the field of the most promising complex sulfides CdZnS, AgInS, CuInS, ZnInS and the predicted scope of their practical application in the article. The tendencies in the research for physicochemical properties of complex metal sulphides are revealed.

Key words: complex metal sulfides, doping, quantum dot, quantum transition, photoluminescence, electrochemical properties, phase transitions, traps, optical properties, solar cells, LEDs.

There are extensive series of creating new materials research based on the synthesis of complex sulfide compounds has been conducted over the past 3 years. It will be presented examples of research in the field of the most promising complex sulfides CdZnS, AgInS, CuInS, ZnInS.

1. Research in the field of complex sulfide CdZnS.

«Structural, optical and photovoltaic properties of Co (3%): CdZnS nanoparticles» [37]. In the present study, CdZnS and Co (3%): CdZnS nanoparticles (NPs) have been synthesized via wet chemical method at room temperature using 1-thioglycerol as a capping agent. The incident photon-to-current conversion efficiency (IPCE) measurement has been carried out for Co (5%): CdZnS for the first time in this study. The results show that Co (3%): CdZnS can be utilized as sensitizers to improve the performance of solar cells. In addition to the photovoltaic properties; structural, optical and morphological properties of Co (3%): CdZnS NPs have been investigated. The results indicate that Co (3%): CdZnS NPs can be suitable material for photovoltaic applications.

«Influence of Ce³⁺ doping on the optical and photocatalytic properties of Zn_{0.8}Cd_{0.2}S-ethylenediamine hybrid nanosheets» [8]. The Ce³⁺-doped Zn_{0.8}Cd_{0.2}S-ethylenediamine (En) hybrid nanosheets were successfully synthesized by a simple solvothermal method and characterized by scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), UV-vis diffusion reflectance spectroscopy (UV-vis DRS) and room-temperature photoluminescence spectra (PL). The effects of Ce³⁺ doping amount on the photo-absorption properties and photocatalytic H₂ evolution rates under visible light irradiation over Zn_{0.8}Cd_{0.2}S-En hybrid nanosheets were also investigated. The results show that the incorporation of Ce³⁺, existing in the form of Ce₂S₃ with uniformly distribution in sample can narrow the band gap, enhance the photo-absorption and extend the photo-absorption range of the Zn_{0.8}Cd_{0.2}S-En hybrid nanosheets. The photocatalytic activity tests prove that Ce³⁺-doped Zn_{0.8}Cd_{0.2}S-En nanosheets have much higher photocatalytic hydrogen production activity when compared with the undoped one. Under the irradiation of visible light, the highest photocatalytic hydrogen production rate of 229.2 $\mu\text{mol h}^{-1}$ is observed over 0.1 wt.% Ce³⁺-doped Zn_{0.8}Cd_{0.2}S-En nanosheets, which is about 1.4

times higher than that of the undoped $\text{Zn}_{0.8}\text{Cd}_{0.2}\text{S}$ -En nanosheets. The improved photocatalytic activity of Ce-doped samples ascribes to the enhanced photo-response in the visible light region and the efficient separation of electron-hole pairs due to the formation of heterojunction between $\text{Zn}_{0.8}\text{Cd}_{0.2}\text{S}$ -En and Ce_2S_3 .

«Size-dependent structural phase transitions and their correlation with photoluminescence and optical absorption behavior of annealed $\text{Zn}_{0.45}\text{Cd}_{0.55}\text{S}$ quantum dots» [46]. In this paper, we investigate the effect of thermally induced structural phase transitions on the photoluminescence (PL) and optical absorption behaviour of $\text{Zn}_{0.45}\text{Cd}_{0.55}\text{S}$ nanoparticles (NPs). Analysis of X-ray diffraction (XRD) patterns and high-resolution electron microscope (HRTEM) images reveal that the as-synthesized sample possesses zinc-blende-type cubic structure. In addition, at annealing temperature (T-a) 400 degrees C, the cubic structure transforms completely into the wurtzite-type hexagonal structure. Furthermore, the second phase transition of the as-synthesized sample has observed at 700 degrees C, where the cubic structure has transformed into mixed polycrystalline phases of hexagonal ZnO, cubic CdO, monoclinic CdSO_3 , and orthorhombic ZnSO_4 structures. These new phases have also confirmed from the analysis of Raman and FTIR spectra. Analysis of UV-visible optical absorption spectra demonstrates that Increasing T-a results in the decrease of optical band gap due the improvement in crystallinity accompanied by the increase in the particle size. The PL emission bands at an excitation energy of 3.818 eV exhibit redshift and a decrease in the intensity with increasing T-a up to 500 degrees C. Meanwhile, further increase in T-a up to 700 degrees C results in the enhancement of green emission intensity. On the other hand, PL emission spectra at 3.354 eV and T. 700 degrees C, reveal a dramatic increase in the emission intensity nearly by one-order of magnitude with respect to its value of the as-synthesized sample. This behaviour is ascribed to the incorporation of oxygen-related defects via thermal annealing in air, which act as additive radiative centers. Also, we have interpreted the observed spectral blue shift of PL emission spectrum with increasing excitation energy.

A similar study of this complex sulfide is also reflected in the following works [11, 32] and in earlier studies [38, 23, 29].

2. Research in the field of complex AgInS sulfide.

«Luminescence and photoelectrochemical properties of size-selected aqueous copper-doped Ag-In-S quantum dots» [47]. Ternary luminescent copper and silver indium sulfide quantum dots (QDs) can be an attractive alternative to cadmium and lead chalcogenide QDs. The optical properties of Cu-In-S and Ag-In-S (AIS) QDs vary over a broad range depending on the QD composition and size. The implementation of ternary QDs as emitters in bio-sensing applications can be boosted by the development of mild and reproducible syntheses directly in aqueous solutions as well as the methods of shifting the photoluminescence (PL) bands of such QDs as far as possible into the near IR spectral range. In the present work, the copper-doping of aqueous non-stoichiometric AIS QDs was found to result in a red shift of the PL band maximum from around 630 nm to similar to 780 nm and PL quenching. The deposition of a ZnS shell results in PL intensity recovery with the highest quantum yield of 15%, with almost not change in the PL band position, opposite to the undoped AIS QDs. Size-selective precipitation using 2-propanol as a non-solvent allows discrimination of up to 9 fractions of Cu-doped AIS/ZnS QDs with the average sizes in the fractions varying from around 3 to 2 nm and smaller and with reasonably the same composition irrespective of the QD size. The decrease of the average QD size results in a blue PL shift yielding a series of bright luminophors with the emission color varies from deep-red to bluish-green and the PL efficiency increases from 11% for the first fraction to up to 58% for the smallest Cu-doped AIS/ZnS QDs. The rate constant of the radiative recombination of the size-selected Cu-doped AIS/ZnS QDs revealed a steady growth with the QD size decrease as a result of the size-dependent enhancement of the spatial exciton confinement. The copper doping was found to result in an enhancement of the photoelectrochemical activity of CAIS/ZnS QDs introduced as spectral sensitizers of mesoporous titania photoanodes of liquid-junction solar cells.

«Origin and Dynamics of Highly Efficient Broadband Photoluminescence of Aqueous Glutathione-Capped Size-Selected Ag-In-S Quantum Dots» [51]. The 2-3 nm size-selected glutathione-capped Ag In S (AIS) and core/shell AIS/ZnS quantum dots (QDs) were produced by precipitation/redissolution from an aqueous colloidal ensemble. The QDs reveal broadband photoluminescence (PL) with a quantum yield of up to 60% for the most populated fraction of the core/shell AIS/ZnS QDs. The PL band shape can be described by a self-trapped exciton model implying the PL band being a sequence of phonon replica of a zero-phonon line resulting from strong electron phonon interaction and a partial conversion of the electron

excitation energy into lattice vibrations. It can be concluded that the position and shape of the PL bands of MS QDs originate not from energy factors (depth and distribution of trap states) but rather from the dynamics of the electron phonon interaction and the vibrational relaxation in the QDs. The rate of vibrational relaxation of the electron excitation energy in MS QDs is found to be size-dependent, increasing almost twice from the largest to the smallest QDs.

«Synthesis of AgInS₂ quantum dots with tunable photoluminescence for sensitized solar cells» [14]. Synthesis of quantum dots (QDs) with high photoluminescence is critical for quantum dot sensitized solar cells (QDSCs). A series of high quality AgInS₂ QDs were synthesized under air circumstance by the organometallic high temperature method. Feature of tunable photoluminescence of AgInS₂ QDs with long lifetime and quantum yields beyond 40% has been achieved, which was mainly attributed to the donor-acceptor pair recombination, contributed above 91% to the whole emission profiles. After ligand exchange with bifunctional linker, water-soluble AgInS₂ QDs were adopted as light harvesters to fabricate QDSCs, achieved best PCE of 2.91% (short-circuit current density of 13.78 mA cm⁻²), open-circuit voltage of 0.47 V, and fill factor of 45%) under one full sun illumination. The improved photovoltaic performance of AgInS₂ QDs-based QDSCs is mainly originated from broadened optoelectronic response range up to 900 nm, and enhanced photoluminescence with long lifetime and high quantum yield beyond 40%, which provide strong photoresponse similar to 40% over the window below 750 nm. The synthetic approach combined with intrinsic defects created by intentionally composition modulation introduces a new approach towards the goal of high performance QDSCs.

The research results of this complex compound are also reflected in the following works [36, 22] in earlier studies [27].

3. Research in the field of complex CuInS₂ sulfide.

«Defect Luminescence from Wurtzite CuInS₂ Nanocrystals: Combined Experimental and Theoretical Analysis» [45]. CuInS₂ nanocrystals with the wurtzite structure show promise for applications requiring efficient energy transport due to their anisotropic crystal structure. We investigate the source of photoluminescence in the near-infrared spectral region recently observed from these nanocrystals. Spectroscopic studies of both wurtzite CuInS₂ itself and samples alloyed with Cd or Zn allow the assignment of this emission to a radiative point defect within the nanocrystal structure. Further, by varying the organic passivation layer on the material, we are able to determine that the atomic species responsible for nonradiative decay paths on the nanocrystal surface are Cu- or S-based. Density functional theory calculations of defect states within the material allow identification of the likely radiative species. Understanding both the electronic structure and optical properties of wurtzite CuInS₂ nanocrystals is necessary for their efficient integration into potential biological, photovoltaic, and photo catalytic applications.

«Interplay between Surface Chemistry, Precursor Reactivity, and Temperature Determines Outcome of ZnS Shelling Reactions on CuInS₂ Nanocrystals» [10]. ZnS shelling of I-III-VI₂ nanocrystals (NCs) invariably leads to blue-shifts in both the absorption and photoluminescence spectra. These observations imply that the outcome of ZnS shelling reactions on I-III-VI₂ colloidal NCs results from a complex interplay between several processes taking place in solution, at the surface of, and within the seed NC. However, a fundamental understanding of the factors determining the balance between these different processes is still lacking. In this work, we address this need by investigating the impact of precursor reactivity, reaction temperature, and surface chemistry (due to the washing procedure) on the outcome of ZnS shelling reactions on CuInS₂ NCs using a seeded growth approach. We demonstrate that low reaction temperatures (150 degrees C) favor etching, cation exchange, and alloying regardless of the precursors used. Heteroepitaxial shell overgrowth becomes the dominant process only if reactive S- and Zn-precursors (S-ODE/OLAM and ZnI₂) and high reaction temperatures (210 degrees C) are used, although a certain degree of heterointerfacial alloying still occurs. Remarkably, the presence of residual acetate at the surface of CIS seed NCs washed with ethanol is shown to facilitate heteroepitaxial shell overgrowth, yielding for the first time CIS/ZnS core/shell NCs displaying red-shifted absorption spectra, in agreement with the spectral shifts expected for a type-I band alignment. The insights provided by this work pave the way toward the design of improved synthesis strategies to CIS/ZnS core/shell and alloy NCs with tailored elemental distribution profiles, allowing precise tuning of the optoelectronic properties of the resulting materials.

The research results of this complex compound are also reflected in the following works [31] in earlier studies [3, 24, 40, 18, 19, 13, 9, 28, 35, 12].

4. Research in the field of complex ZnInS sulfide.

«Improving the emission of ultrasmall Mn-doped ZnInS quantum dots via Ag-induced trap state energy level» [39]. For ultrasmall Mn-doped quantum dots (QDs), the energy transfer of the exciton to the Mn is the key factor for Mn emission. Herein, the Ag-induced electron trap state energy level, which is an intermediate energy level between the conduction band (CB) and T-4(1) of Mn, is proposed for improving the energy transfer. After doping the Ag and forming Ag&Mn:ZnInS QDs, most excitons will first be captured by the intermediate energy level and then be transferred to Mn d-states, leading to enhanced photoluminescence (PL) quantum yields (QY) of the QDs from the original 17% (Mn:ZnInS QDs) to 30% (Ag&Mn:ZnInS QDs).

«Dopant-controlled photoluminescence of Ag-doped Zn-In-S nanocrystals» [50]. In this work, we reported the growth of cadmium-free Ag-doped Zn-In-S nanocrystals (NCs) with effective photoluminescence (PL) via a hot-injection strategy. The effects of the nucleation temperatures, reaction times, and Ag-doping concentrations on the PL properties of Ag-doped Zn-In-S NCs were investigated systematically. The as-synthesized NCs exhibit color-tunable PL emissions covering a broad visible range of 472-585 nm. After being passivated by a protective ZnS shell, the PL quantum yield (QY) of the resultant NCs was greatly improved up to 33%. With the increase of the Ag-doping level, the PL is significantly intensified due to the improved concentration of Ag ions which provides more holes to recombine with electrons from the bottom of the conduction band. This also makes the emission via the dopant energy level become a powerful, competitive advantage for the NCs with higher Ag-doping levels, resulting in a longer lifetime and higher PL QY. These results suggest that tailoring the Ag-doping level can be a powerful strategy to control the optical properties of Ag-doped Zn-In-S NCs.

«Highly bright and stable white-light-emitting cadmium-free Ag, Mn co-doped Zn-In-S / ZnS quantum dots and their electroluminescence» [55]. Optimized white light emitting Ag, Mn:Zn-In-S quantum dots (QDs) were synthesized via a simple, scalable, reproducible, and low-cost one-pot non-injection synthetic approach. After coating a thick ZnS shell (similar to 12 monolayers) on the core QDs, high photoluminescence (PL) quantum yield (QY) up to 76% was achieved and high emission efficiency was retained even when the initially oil-soluble QDs were transferred into aqueous media by ligand replacement. Moreover, both thermal stability and photostability of thick shell-Ag, Mn:Zn-In-S/ZnS QDs were significantly enhanced as compared with those of Ag, Mn:Zn-In-S core QDs due to the suppressed surface defects resulting from the passivation of the dense ZnS layers. White quantum dot light-emitting diodes (QD-LEDs) were fabricated using thick shell Ag, Mn:Zn-In-S/ZnS QDs as single QDs emitter, showing good performance with maximum current efficiency of 1.86 cd A(-1) corresponding to external quantum efficiency (EQE) of 0.82% at a current density of 0.065 mA cm(-2), color rendering indices (CRI) of 83, Commission International d'Eclairage (CIE) coordinates of (0.344, 0.393) and correlated color temperature (CCT) of 5156 K.

«Doping concentration-dependent photoluminescence properties of Mn-doped Zn-In-S quantum dots» [15]. In this report, doping concentration-dependent photoluminescence (PL) properties of Mn-doped ternary Zn-In-S quantum dots (QDs) were studied by using steady-state and time-resolved PL spectroscopy. The QDs PL was firstly significantly intensified with the increasing Mn doping concentration and then decreased after the doping concentration increased up to 7.5 at.%. However, their decay lifetimes exhibit a monotone decrease with Mn doping concentration ranged from 0 to 10 at.%. It can be concluded that the PL intensity was mainly determined by two factors: one was the increased efficiency of energy transfer from host excitons to Mn²⁺ ion acceptor, and the other was the decreased efficiency of the emission from a Mn²⁺ ion, which was caused by the increased component of exposed Mn²⁺ ions on QDs surface and the accelerated interaction between adjacent dopants. The competition of above two exciton relaxation dynamics processes determined the trend of the PL intensity, while the latter was responsible for the monotonously decreased lifetime of the Mn²⁺ ion emission with the increasing Mn doping concentration.

The research results of this complex compound are also reflected in the following works [16, 17] in earlier studies [25, 26, 34, 1, 2].

Note that other complex compounds of complex ternary sulfides such as CdPbS [7], HgPbS [20], BaPbS [21], CdCoS [4], PbZnS [5], PbCoS [6], HgCdS [30], CdSnS [33], PbCaS [49], CdPbS [52], PbSnS [53], ZnMnS [41], CdMnS [43], ZnCoS [42], CdFeS [54], CdNiS [44], MnZnS [48] were studied.

Research in the field of sulfides was also carried out by domestic scientists. For example, studies for ZnS sulfides are reflected in [56, 57], and the study for the physicochemical properties of CdS sulfides is described in [58, 59]. Practical applications of complex sulfides are described in [60].

Findings

There a clear tendency of doping the basic sulfide material with various chemical elements that are not part of them is followed from the analysis of the vast majority of modern works (on the synthesis and study of complex sulfides) shown in the literature review. This operation significantly changes the physico-chemical properties of complex sulfide, which, as a result, leads to a significant expansion of their practical application in science and technology.

М.Ә. Дәуренбек¹, А.К. Мажипбаев², А.А. Бакибаев³

¹М.Х. Дулати атындағы Тараз мемлекеттік университеті, Тараз қ., Қазақстан;

²Тараз мемлекеттік педагогикалық университеті, Тараз қ., Қазақстан;

³Томск ұлттық зерттеу университеті, Томск қаласы, Томск облысы, Ресей

КҮРДЕЛІ СУЛЬФИДТІ ҚОСЫЛЫСТАР САЛАСЫНДАҒЫ ЗАМАНАУИ ЗЕРТТЕУЛЕР ТУРАЛЫ (ЖАҒДАЙЫ ЖӘНЕ БЕТАЛЫСЫ)

Аннотация. Мақалада күрделі сульфидтерді зерттеу бойынша бір бөлігі мақалада келтірілген 600 аса әдебиеттік көздердің ең маңызды ғылыми еңбектеріне шолу жасалынды. Ең перспективалы күрделі сульфидтер CdZnS, AgInS, CuInS, ZnInS саласына мысалдар және олардың тәжірибелік қолданылатын болжамды ауқымы келтірілді.

Осылайша, CdZnS күрделі сульфид саласындағы зерттеулер бойынша жарық энергиясын электр тогына түрлендіру тиімділігі анықталды, бұл осы қосылысты күн элементтерінің сипаттамаларын жақсарту үшін сенсбилизатор ретінде пайдалану туралы айтуға мүмкіндік береді. Ce_2S_3 түріндегі Ce^{3+} -ді тегіс бөліп қосу тыйым салынған аймақтың енін тарылтып, $\text{Zn}_{0.8}\text{Cd}_{0.2}\text{S}$ гибриді наножапырақтардың фото сіңіру диапазонын ұлғайтуы және кеңейтуі мүмкін. $\text{Zn}_{0.45}\text{Cd}_{0.55}\text{S}$ нанобөлшектерді оптикалық сіңіру және фотолюминесценциясына термиялық индукцияланған құрылымдық фазалық ауысулардың әсері зерттелді.

AgInS аралас сульфид саласындағы зерттеулерде мыспен легирленуі сұйық өтумен күн элементтеріндегі титан диоксидінің мезокеуекті фотоанодтардың спектрлік сенсбилизаторлары ретінде енгізілген CAIS/ZnS кванттық нүктелерінің фотоэлектрхимиялық белсенділігінің жоғарылауына алып келетіні байқалған. Кванттық нүктелердің фотолюминесценция жолақтарының орналасуы мен пішіні энергетикалық факторлармен емес (тұзақтардың тереңдігімен және жай-күйінің таралуымен), электрондардың фонондармен өзара әрекеттесу динамикасымен және кванттық нүктелерде тербелмелі релаксациямен байланысты екендігі туралы қорытынды жасалады. Жоғары фотолюминесценциялы кванттық нүктелердің синтезі күн элементтері үшін шешуші мәнге ие болатыны атап көрсетілді.

CuInS₂ күрделі сульфид саласындағы зерттеулер бойынша жұмыстарда CuInS₂ вюрциттің өзін және Cd немесе легирленген Zn үлгілердің спектроскопиялық зерттеулері бұл сәулеленуді нанокристаллдағы радиациялық нүктелік ақауға жатқызуға мүмкіндік беретіні дәлелденген. Өңдеу әдісімен CuInS₂ нанокристалдарындағы ZnS қабыршықтану реакцияларының қорытынды мәселесі прекурсордың реакциялық қабілеттілігінің, реакция температурасының және беттің химиялық құрамының әсерлерін зерттеу арқылы шешіледі.

ZnInS аралас сульфидті зерттеу кезінде легирленген Mn аса аз кванттық нүктелер үшін экситонмен энергияны Mn-ге тасымалдау негізгі фактор болып табылады. Ыстық инжекция әдісімен тиімді фотолюминесценциясы бар, құрамында кадмий жоқ легирленген Ag-ң ZnInS нанокристаллдарының өсуі зерттелді. Ақ жарық сәуле шығаратын оңтайландырылған кванттық нүктелер Ag, Mn белгіленді: ZnInS инжекциясыз қарапайым, масштабталған, жаңғыртылған және қымбат емес синтетикалық тәсіл арқылы синтезделді. Спектроскопияны пайдалана отырып, Mn легирленген ZnInS-ң фотолюминесцентті қасиеттері, үштік кванттық нүктелері зерттелді.

Шолуда келтірілген әдеби көздерді талдаудан, күрделі сульфидтерді синтездеу және зерттеу жөніндегі қазіргі заманғы жұмыстардың басым көпшілігінде сульфидтің негізгі материалын олардың құрамына кірмейтін әртүрлі химиялық элементтермен қоспалау үрдісі айқын байқалады. Бұл операция өз кезегінде

ғылым мен техникада практикалық қолдану аясын айтарлықтай кеңейтуге әкелетін күрделі сульфидтің физика-химиялық қасиеттерін айтарлықтай өзгертеді.

Түйін сөздер: металдардың күрделі сульфидтері, қоспалау, кванттық нүкте, кванттық ауысу, фотолюминесценция, электрохимиялық қасиеттері, фазалық ауысулар, тұтқыштар, оптикалық қасиеттері, күн батареялары, жарық диодтары.

М.Ә. Дәуренбек¹, А.К. Мажобаев², А.А. Бакибаев³

¹Таразский государственный университет им. М.Х. Дулати, Тараз, Казахстан;

²Таразский государственный педагогический университет, Тараз, Казахстан;

³Национальный исследовательский Томский государственный университет, Томск, Томская область, Россия

О СОВРЕМЕННЫХ ИССЛЕДОВАНИЯХ В ОБЛАСТИ СЛОЖНЫХ СУЛЬФИДНЫХ СОЕДИНЕНИЙ (СОСТОЯНИЕ И ТЕНДЕНЦИИ)

Аннотация. В статье сделан обзор наиболее значимых научных работ по исследованию сложных сульфидов из более 600 литературных источников, часть которых приведена в статье. Приведены примеры исследований в области наиболее перспективных сложных сульфидов CdZnS, AgInS, CuInS, ZnInS и прогнозируемая сфера их практического применения.

Так, по исследованиям в области сложного сульфида CdZnS выявлена эффективность преобразования световой энергии в электрический ток, что позволяет судить об использовании этого соединения в качестве сенсibilизатора для улучшения характеристик солнечных элементов. Отмечается, что включение Ce^{3+} , существующего в форме Ce_2S_3 с равномерным распределением в образце может сузить ширину запрещенной зоны, увеличить и расширить диапазон фотопоглощения гибридных наночастиц $\text{Zn}_{0,8}\text{Cd}_{0,2}\text{S}$. Исследовано влияние термически индуцированных структурных фазовых переходов на фотолюминесценцию и оптическое поглощение наночастиц $\text{Zn}_{0,45}\text{Cd}_{0,55}\text{S}$.

В исследованиях в области смешанного сульфида AgInS отмечается, что легирование медью приводит к повышению фотоэлектрохимической активности квантовых точек CAIS / ZnS, введенных в качестве спектральных сенсibilизаторов мезопористых фотоанодов диоксида титана в солнечных элементах с жидким переходом. Делается вывод о том, что положение и форма полос фотолюминесценции квантовых точек обусловлены не энергетическими факторами (глубиной и распределением состояний ловушек), а, скорее, динамикой взаимодействия электронов с фононами и колебательной релаксацией в квантовых точках. Отмечено, что синтез квантовых точек с высокой фотолюминесценцией имеет решающее значение для солнечных элементов.

В работах по исследованиям в области сложного сульфида CuInS₂ доказано, что спектроскопические исследования как самого вюрцита CuInS₂, так и образцов, легированных Cd или Zn, позволяют отнести это излучение к радиационному точечному дефекту в нанокристалле. Проблема исхода реакций шелушения ZnS на нанокристаллах CuInS₂ методом травления решается исследованием влияния взаимодействий реакционной способности прекурсора, температуры реакции и химического состава поверхности.

При исследованиях смешанного сульфида ZnInS выявлено, что для сверхмалых квантовых точек, легированных Mn, передача энергии эксцитонном в Mn является ключевым фактором. Исследован рост нанокристаллов ZnInS, легированных Ag, не содержащих кадмия с эффективной фотолюминесценцией методом горячей инъекции. Отмечено, что оптимизированные излучающие белый свет квантовые точки Ag, Mn: ZnInS были синтезированы с помощью простого, масштабируемого, воспроизводимого и недорогого синтетического подхода без инъекции. Изучены фотолюминесцентные свойства, тройных квантовых точек ZnInS, легированных Mn, с использованием спектроскопии.

Из анализа литературных источников, приведённых в обзоре, следует, что в подавляющем большинстве современных работ по синтезу и исследованию сложных сульфидов явно прослеживается тенденция легирования основного материала сульфида различными химическими элементами, не входящих в их состав. Эта операция заметно изменяет физико-химические свойства сложного сульфида, что, как следствие, в свою очередь приводит к значительному расширению сферы их практического применения в науке и технике.

Ключевые слова: сложные сульфиды металлов, легирование, квантовая точка, квантовый переход, фотолюминесценция, электрохимические свойства, фазовые переходы, ловушки, оптические свойства, солнечные батареи, светодиоды.

Information about the authors:

Daurenbek Murat Amiruly – PhD student of specialty chemistry of the Chemistry & chemical technology department, M.H. Dulaty Taraz state university, Suleimenov str., 7, Taraz, Kazakhstan, e-mail: mdaurenbek@mail.ru, <https://orcid.org/0000-0003-3275-2920>;

Mazhibaev Asylzhan Kenzhekereevich – candidate of chemistry sciences, department of Chemistry & chemistry teaching methods, Taraz state pedagogical university, Tole bi str., 62, Taraz, Kazakhstan, e-mail: 707olo@mail.ru, <https://orcid.org/0000-0001-8997-9646>;

Bakibaev Abdigali Abdimanapovich – doctor of chemistry sciences, professor, leading researcher, laboratory of catalytic research, National research Tomsk State University, Tomsk, Tomsk region, Russia, e-mail: bakibaev@mail.ru, <https://orcid.org/0000-0002-3335-3166>

REFERENCES

[1] ANAGNOSTOPOULOS A, KAMBAS K, SPYRIDELIS J (1986) ON THE OPTICAL AND ELECTRICAL-PROPERTIES OF THE ZN₃IN₂S₆ LAYERED COMPOUND. *Materials research bulletin*, 21 (4):407-413. DOI: 10.1016/0025-5408(86)90005-X (in Eng).

[2] ANDREANI F, ROMEO N (1976) PREPARATION AND PROPERTIES OF ZNIN₂S₄ THIN-FILMS. *Thin solid films*, 31 (3):217-221. DOI: 10.1016/0040-6090(76)90368-0 (in Eng).

[3] Asgary S, Mirabbaszadeh K, Nayebi P, Emadi H (2014) Synthesis and investigation of optical properties of TOPO-capped CuInS₂ semiconductor nanocrystal in the presence of different solvent. *Materials research bulletin*, 51:411-417. DOI: 10.1016/j.materresbull.2013.12.059 (in Eng).

[4] Bacaksiz E, Tomakin M, Altunbas M, Parlak M, Colakoglu T (2008) Structural, optical and magnetic properties of Cd(1-x)CoxS thin films prepared by spray pyrolysis. *Physica B condensed matter*, 403 (19-20):3740-3745. DOI: 10.1016/j.physb.2008.07.006 (in Eng).

[5] Badawi, A, Al Otaibi, AH, Albaradi AM, Al-Hosiny N, Alomairy SE (2018) Tailoring the energy band gap of alloyed Pb_{1-x}Zn_xS quantum dots for photovoltaic applications. *Journal of materials science-materials in electronics*, 29 (24):20914-20922. DOI: 10.1007/s10854-018-0235-2 (in Eng).

[6] Badawi, A (2019) Tunable energy band gap of Pb_{1-x}CoxS quantum dots for optoelectronic applications. *Superlattices and microstructures*, 125:237-246. DOI: 10.1016/j.spmi.2018.11.012 (in Eng).

[7] Badawi A (2016) Photoacoustic study of alloyed Cd_{1-x}Pb_xS quantum dots sensitized solar cells electrodes. *Journal of materials science-materials in electronics*, 27 (8):7899-7907. DOI: 10.1007/s10854-016-4781-1 (in Eng).

[8] Bai YH, Wang K, Wang XT (2018) Influence of Ce³⁺ doping on the optical and photocatalytic properties of Zn_{0.8}Cd_{0.2}S-ethylenediamine hybrid nanosheets. *Journal of photochemistry and photobiology A-chemistry*, 356:355-363. DOI:10.1016/j.jphotochem.2018.01.014 (in Eng).

[9] Banger KK, Cowen J, Hepp AF (2001) Synthesis and characterization of the first liquid single-source precursors for the deposition of ternary chalcopyrite (CuInS₂) thin film materials. *Chemistry of materials*, 13 (11): 3827-3829. DOI: 10.1021/cm010507o (in Eng).

[10] Berends AC, van der Stam W, Hofmann JP, Bladt E, Meeldijk JD, Bals S, Donega CD (2018) Interplay between Surface Chemistry, Precursor Reactivity, and Temperature Determines Outcome of ZnS Shelling Reactions on CuInS₂ Nanocrystals. *Chemistry of materials*, 30 (7):2400-2413. DOI: 10.1021/acs.chemmater.8b00477 (in Eng).

[11] Boltaev GS, Fu DJ, Sobirov BR, Smirnov MS, Ovchinnikov OV, Zvyagin AI, Ganeev RA (2018) Optical limiting, nonlinear refraction and nonlinear absorption of the associates of Cd_{0.5}Zn_{0.5}S quantum dots and dyes. *Optics express*, 26 (11):13865-13875. DOI: 10.1364/OE.26.013865 (in Eng).

[12] Braunger D, Hariskos D, Walter T, Schock HW (1996) An 11.4% efficient polycrystalline thin film solar cell based on CuInS₂ with a Cd-free buffer layer. *Solar energy materials and solar cells*, 40 (2):97-102. DOI: 10.1016/0927-0248(95)00069-0 (in Eng).

[13] Bu XH, Zheng NF, Li YQ, Feng PY (2002) Pushing up the size limit of chalcogenide supertetrahedral clusters: Two- and three-dimensional photoluminescent open frameworks from (Cu₅In₃O₅S₄)(13-) clusters. *Journal of the American chemical society*, 124 (43):12646-12647. DOI: 10.1021/ja021009z (in Eng).

[14] Cai CQ, Zhai LL, Ma YH, Zou C, Zhang LJ, Yang Y, Huang SM (2017) Synthesis of AgInS₂ quantum dots with tunable photoluminescence for sensitized solar cells. *Journal of power sources*, 341:11-58. DOI: 10.1016/j.jpowsour.2016.11.101 (in Eng).

[15] Cao S, Zheng JJ, Dai CC, Wang L, Li CM, Yang WY, Shang MH (2018) Doping concentration-dependent photoluminescence properties of Mn-doped Zn-In-S quantum dots. *Journal of materials science*, 53 (2):1286-1296. DOI:10.1007/s10853-017-1598-0 (in Eng).

[16] Cao S, Zheng JJ, Zhao JL, Yang ZB, Shang MH, Li CM, Yang WY, Fang XS (2016) Robust and Stable Ratiometric Temperature Sensor Based on Zn-In-S Quantum Dots with Intrinsic Dual-Dopant Ion Emissions. *Advanced functional materials*, 26 (40): 7224-7233. DOI:10.1002/adfm.201603201 (in Eng).

[17] Cao S, Zhao JL, Yang WY, Li CM, Zheng JJ (2015) Mn²⁺-doped Zn-In-S quantum dots with tunable bandgaps and high photoluminescence properties. *Journal of materials chemistry c*, 3 (34):8844-8851. DOI: 10.1039/c5tc01370d (in Eng).

- [18] Castro SL, Bailey SG, Raffaele RP, Banger KK, Hepp AF (2004) Synthesis and characterization of colloidal CuInS₂ nanoparticles from a molecular single-source precursor. *Journal of physical chemistry B*, 108 (33):12429-12435. DOI: 10.1021/jp049107p (in Eng).
- [19] Castro SL, Bailey SG, Raffaele RP, Banger KK, Hepp AF (2003) Nanocrystalline chalcopyrite materials (CuInS₂ and CuInSe₂) via low-temperature pyrolysis of molecular single-source precursors. *Chemistry of materials*, 15 (16):3142-3147. DOI: 10.1021/cm034161o (in Eng).
- [20] Chattarki AN, Maldar NN, Deshmukh LP (2014) Synthesis, structure and spectro-microscopic studies of polycrystalline Hg_xPb_{1-x}S thin films grown by a chemical route. *Journal of alloys and compounds*, 597:223-229. DOI: 10.1016/j.jallcom.2014.01.006 (in Eng).
- [21] Chattopadhyaya S, Bhattacharjee R (2017) Theoretical study of structural, electronic and optical properties of BaxPb_{1-x}S, BaxPb_{1-x}Se and BaxPb_{1-x}Te ternary alloys using FP-LAPW approach. *Journal of alloys and compounds*, 694:1348-1364. DOI: 10.1016/j.jallcom.2016.10.096 (in Eng).
- [22] Chen SQ, Demillo V, Lu MG, Zhu XS (2016) Preparation of photoluminescence tunable Cu-doped AgInS₂ and AgInS₂/ZnS nanocrystals and their application as cellular imaging probes. *RSC advances*, 6 (56):51161-51170. DOI: 10.1039/c6ra09494e (in Eng).
- [23] Chen ZG, Tian QW, Song YL, Yang JM, Hu JQ (2010) One-pot synthesis of Zn_xCd_{1-x}S nanocrystals with tunable optical properties from molecular precursors. *Journal of alloys and compounds*, 506 (2):804-810. DOI: 10.1016/j.jallcom.2010.07.075 (in Eng).
- [24] Chen BK, Zhong HZ, Wang MX, Liu RB, Zou BS (2013) Integration of CuInS₂-based nanocrystals for high efficiency and high colour rendering white light-emitting diodes. *Nanoscale*, 5(8): 3514-3519. DOI: 10.1039/c3nr33613a (in Eng).
- [25] Chen ZX, Li DZ, Zhang WJ, Shao Y, Chen TW, Sun M, Fu XZ (2009) Photocatalytic Degradation of Dyes by ZnIn₂S₄ Microspheres under Visible Light Irradiation. *Journal of physical chemistry c*, 113 (11): 4433-4440. DOI: 10.1021/jp8092513 (in Eng).
- [26] Chen ZX, Li DZ, Zhang WJ, Chen C, Li WJ, Sun M, He YH, Fu XZ (2008) Low-Temperature and Template-Free Synthesis of ZnIn₂S₄ Microspheres. *Inorganic chemistry*, 47 (21): 9766-9772. DOI: 10.1021/ic800752t (in Eng).
- [27] Cheng KC, Law WC, Yong KT, Nevins JS, Watson DF, Ho HP, Prasad PN (2011) Synthesis of near-infrared silver-indium-sulfide (AgInS₂) quantum dots as heavy-metal free photosensitizer for solar cell applications. *Chemical physics letters*, 515 (4-6):254-257. DOI: 10.1016/j.cplett.2011.09.027 (in Eng).
- [28] Czekelius C, Hilgendorff M, Spanhel L, Bedja I, Lerch M, Muller G, Bloeck U, Su DS, Giersig M (1999) A simple colloidal route to nanocrystalline ZnO/CuInS₂ bilayers. *Advanced materials*, 11 (8):643-646. DOI: 10.1002/(SICI)1521-4095(199906)11:8<643::AID-ADMA643>3.0.CO;2-I (in Eng).
- [29] Dai J, Jian WP, Zhuang JQ, Yang WS (2006) Synthesis and optical properties of Zn_xCd_{1-x}S : Ag nanocrystals. *Chemical journal of Chinese universities - Chinese*, 27 (4): 704-707. (in Eng).
- [30] Deshmukh LP, Garadkar KM, Sutrave DS (1998) Studies on solution grown Hg_xCd_{1-x}S thin films. *Materials chemistry and physics*, 55 (1):30-35. DOI: 10.1016/S0254-0584(98)00004-2 (in Eng).
- [31] Fuhr AS, Yun HJ, Makarov NS, Li HB, McDaniel H, Klimov VI (2017) Light Emission Mechanisms in CuInS₂ Quantum Dots Evaluated by Spectral Electrochemistry. *ACS photonics*, 4 (10): 2425-2435. DOI: 10.1021/acsp Photonics.7b00560 (in Eng).
- [32] Ghosh S, Sarkar S, Das BK, Sen D, Samanta M, Chattopadhyay KK (2017) Band edge tuned Zn_xCd_{1-x}S solid solution nanopowders for efficient solar photocatalysis. *Physical chemistry chemical physics*, 19 (44):29998-30009. DOI: 10.1039/c7cp06305a (in Eng).
- [33] Ghosh PK, Maiti UN, Ahmed SF, Chattopadhyay KK (2006) Highly conducting transparent nanocrystalline Cd_{1-x}S_xS thin film synthesized by RF magnetron sputtering and studies on its optical, electrical and field emission properties. *Solar energy materials and solar cells*, 90 (16): 2616-2629. DOI: 10.1016/j.solmat.2006.02.015 (in Eng).
- [34] Gou XL, Cheng FY, Shi YH, Zhang L, Peng SJ, Chen J, Shen PW (2006) Shape-controlled synthesis of ternary chalcogenide ZnIn₂S₄ and CuIn(S,Se)₂ nano-/microstructures via facile solution route. *Journal of the American chemical society*, 128 (22):7222-7229. DOI: 10.1021/ja0580845 (in Eng).
- [35] Gurinovich LI, Gurin VS, Ivanov VA, Bodnar IV, Molochko AP, Solovej NP (1998) Crystal structure and optical properties of CuInS₂ nanocrystals in a glass matrix. *Physica status solidi b – basic solid state physics*, 208 (2):533-540. DOI: 10.1002/(SICI)1521-3951(199808)208:2<533::AID-PSSB533>3.0.CO;2-P (in Eng).
- [36] Hamanaka Y, Ozawa K, Kuzuya T (2014) Enhancement of Donor-Acceptor Pair Emissions in Colloidal AgInS₂ Quantum Dots with High Concentrations of Defects. *Journal of physical chemistry c*, 118 (26):14562-14568. DOI: 10.1021/jp501429f (in Eng).
- [37] Horoz S (2018) Structural, optical and photovoltaic properties of Co (3%): CdZnS nanoparticles. *Indian journal of pure & applied physics*, 56 (10):759-764.
- [38] Hospodkova A, Svoboda L, Praus P (2015) Dependence of photocatalytic activity of Zn_xCd_{1-x}S quantum dot composition. *Chinese journal of catalysis*, 36 (3):328-335. DOI:10.1016/S1872-2067(14)60269-2 (in Eng).
- [39] Huang GG, Wang CL, Xu SH, Cui YP (2017) Improving the emission of ultrasmall Mn-doped ZnInS quantum dots via Ag-induced trap state energy level. *Materials research express*, 4 (8), article number: 085028. DOI:10.1088/2053-1591/aa806c (in Eng).
- [40] Huang WC, Tseng CH, Chang SH, Tuan HY, Chiang CC, Lyu LM, Huang MH (2012) Solvothermal Synthesis of Zincblende and Wurtzite CuInS₂ Nanocrystals and Their Photovoltaic Application. *Langmuir*, 28 (22): 8496-8501. DOI: 10.1021/la300742p (in Eng).

- [41] Ichino K, Misasa H, Kitagawa M, Tanaka S, Kobayashi H (2001) Mechanism of blue-shift of Mn²⁺ luminescence in ZnMgS : Mn for electroluminescent thin films. Japanese journal of applied physics part 1-regular papers short notes & review papers, 40 (3A): 1289-1293. DOI: 10.1143/JJAP.40.1289 (in Eng).
- [42] Kamble, SS, Dubal DP, Tarwal NL, Sikora A, Jang JH, Deshmukh LP (2016) Studies on the Zn_xCo_{1-x}S thin films: A facile synthesis process and characteristic properties. Journal of alloys and compounds, 656:590-597. DOI: 10.1016/j.jallcom.2015.10.011 (in Eng).
- [43] Kim DJ, Choi YD, Lee JW (2011) Investigation of crystal structure and optical properties of Cd_{1-x}MnxS epilayers. Journal of vacuum science & technology A, 29 (5), article number 051504. DOI: 10.1116/1.3610173 (in Eng).
- [44] Kumar S, Sharma P, Sharma V (2013) Phase Transition in II-VI Nanofilms of Dilute Magnetic Semiconductors: Cd_{1-x}NixS. Science of advanced materials, 5 (6):713-717. DOI: 10.1166/sam.2013.1505 (in Eng).
- [45] Leach ADP, Shen X, Faust A, Cleveland MC, La Croix AD, Banin U, Pantelides ST, Macdonald JE (2016) Defect Luminescence from Wurtzite CuInS₂ Nanocrystals: Combined Experimental and Theoretical Analysis. Journal of physical chemistry c, 120 (9):5207-5212. DOI: 10.1021/acs.jpcc.6b00156 (in Eng).
- [46] Osman MA, Abd-Elrahim AG, Othman AA (2018) Size-dependent structural phase transitions and their correlation with photoluminescence and optical absorption behavior of annealed Zn_{0.45}Cd_{0.55}S quantum dots. Materials characterization, 144:247-263. DOI: 10.1016/j.matchar.2018.07.020 (in Eng).
- [47] Raevskaya A, Rozovik O, Novikova A, Selyshchev O, Stroyuk O, Dzhagan V, Goryacheva I, Gaponik N, Zahn DRT, Eychmuller A (2018) Luminescence and photoelectrochemical properties of size-selected aqueous copper-doped Ag-In-S quantum dots. RSC Advances, 8 (14):7550-7557. DOI: 10.1039/c8ra00257f (in Eng).
- [48] Sarkar U, Debnath B, Debbarma M, Ghosh D, Chanda S, Bhattacharjee R, Chattopadhyaya S (2019) Density functional calculations of structural, elastic and optoelectronic features of MgxZn_{1-x}S, MgxZn_{1-x}Se and MgxZn_{1-x}Te alloys. Materials chemistry and physics, 230:54-77. DOI: 10.1016/j.matchemphys.2019.03.050 (in Eng).
- [49] Sifi C, Meradji H, Slimani M, Labidi S, Ghemid S, Hanneche EB, Hassan FE (2009) First principle calculations of structural, electronic, thermodynamic and optical properties of Pb_{1-x}CaxS, Pb_{1-x}CaxSe and Pb_{1-x}CaxTe ternary alloys. Journal of physics condensed matter, 21 (19), article number 195401. DOI: 10.1088/0953-8984/21/19/195401 (in Eng).
- [50] Shi XJ, Zheng JJ, Shang MH, Xie TT, Xie JB, Cao S, Yang WY (2017) Dopant-controlled photoluminescence of Ag-doped Zn-In-S nanocrystals. Journal of materials research, 32 (18):3585-3592. DOI: 10.1557/jmr.2017.247 (in Eng).
- [51] Stroyuk O, Raevskaya A, Spranger F, Selyshchev O, Dzhagan V, Schulze S, Zahn DRT, Eychmuller A (2018) Origin and Dynamics of Highly Efficient Broadband Photoluminescence of Aqueous Glutathione-Capped Size-Selected Ag-In-S Quantum Dots. Journal of physical chemistry c, 122 (25):13648-13658. DOI: 10.1021/acs.jpcc.8b00106 (in Eng).
- [52] Tan GL, Liu LM, Wu WB (2014) Mid-IR band gap engineering of Cd_xPb_{1-x}S nanocrystals by mechanochemical reaction. AIP Advances, 4 (6) DOI: 10.1063/1.4881878 (in Eng).
- [53] Wei H, Su YJ, Chen SZ, Lin Y, Yang Z, Sun H, Zhang YF (2011) Synthesis of ternary Pb_xSn_{1-x}S nanocrystals with tunable band gap. Grystengcomm, 13 (22):6628-6631. DOI: 10.1039/c1ce05999h (in Eng).
- [54] Wu XJ, Shen DZ, Zhang ZZ, Liu KW, Li BH, Zhang JY, Lu YM, Zhao, DX, Yao B, Ren, XG, Fan XW (2007) Characterization of Cd_{1-x}FexS diluted magnetic semiconductors grown at near phase conversion temperature. Solid state communications, 141 (6):344-347. DOI: 10.1016/j.ssc.2006.11.002 (in Eng).
- [55] Zhang WJ, Pan CY, Cao F, Wang HR, Yang XY (2018) Highly bright and stable white-light-emitting cadmium-free Ag, Mn co-doped Zn-In-S / ZnS quantum dots and their electroluminescence. Journal of materials chemistry c, 6 (38):10233-10240. DOI: 10.1039/c8tc03742f (in Eng).
- [56] Баешов А.Б., Қоңырбаев А.Е., Сарбаева М.Т. (2014) Мырыш сульфидін электрохимиялық әдіспен алу, КР ҰҒА ХАБАРЛАРЫ, химия және технология сериясы, 6:44-48.
- [57] Уразов К.А., Дергачёва М.Б., Леонтьева К.А., Хусурова Г.М., Яскевич В.И. (2014) Электрохимическое осаждение плёнок сульфида цинка, ИЗВЕСТИЯ НАН РК, серия химия и технология, 3:36-43.
- [58] Дергачёва М.Б., Леонтьева К.А., Уразов К.А., Хусурова Г.М., Комашко Л.В. (2014) Образование коллоидных растворов CdS, ИЗВЕСТИЯ НАН РК, серия химия и технология, 2:9-13.
- [59] Дергачёва М.Б., Леонтьева К.А., Уразов К.А. (2014) Влияние освещения на электроосаждение CdS, ИЗВЕСТИЯ НАН РК, серия химия и технология, 1:15-20.
- [60] Абдуллин Х.А., Мукашев Б.Н. (2013) Физика полупроводников и наноструктур, ДОКЛАДЫ НАН РК, 3:8-21.

Publication Ethics and Publication Malpractice in the journals of the National Academy of Sciences of the Republic of Kazakhstan

For information on Ethics in publishing and Ethical guidelines for journal publication see <http://www.elsevier.com/publishingethics> and <http://www.elsevier.com/journal-authors/ethics>.

Submission of an article to the National Academy of Sciences of the Republic of Kazakhstan implies that the described work has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis or as an electronic preprint, see <http://www.elsevier.com/postingpolicy>), that it is not under consideration for publication elsewhere, that its publication is approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out, and that, if accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder. In particular, translations into English of papers already published in another language are not accepted.

No other forms of scientific misconduct are allowed, such as plagiarism, falsification, fraudulent data, incorrect interpretation of other works, incorrect citations, etc. The National Academy of Sciences of the Republic of Kazakhstan follows the Code of Conduct of the Committee on Publication Ethics (COPE), and follows the COPE Flowcharts for Resolving Cases of Suspected Misconduct (http://publicationethics.org/files/u2/New_Code.pdf). To verify originality, your article may be checked by the Cross Check originality detection service <http://www.elsevier.com/editors/plagdetect>.

The authors are obliged to participate in peer review process and be ready to provide corrections, clarifications, retractions and apologies when needed. All authors of a paper should have significantly contributed to the research.

The reviewers should provide objective judgments and should point out relevant published works which are not yet cited. Reviewed articles should be treated confidentially. The reviewers will be chosen in such a way that there is no conflict of interests with respect to the research, the authors and/or the research funders.

The editors have complete responsibility and authority to reject or accept a paper, and they will only accept a paper when reasonably certain. They will preserve anonymity of reviewers and promote publication of corrections, clarifications, retractions and apologies when needed. The acceptance of a paper automatically implies the copyright transfer to the National Academy of Sciences of the Republic of Kazakhstan.

The Editorial Board of the National Academy of Sciences of the Republic of Kazakhstan will monitor and safeguard publishing ethics.

Правила оформления статьи для публикации
в журнале смотреть на сайте:

www.nauka-nanrk.kz

<http://chemistry-technology.kz/index.php/en/arhiv>

[ISSN 2518-1491 \(Online\)](#), [ISSN 2224-5286 \(Print\)](#)

Редакторы: *М. С. Ахметова, Г. Б. Халидуллаева, Д. С. Аленов*
Верстка на компьютере *А.М. Кульгинбаевой*

Подписано в печать 13.02.2020.

Формат 60x88¹/₈. Бумага офсетная. Печать – ризограф.
7,8 п.л. Тираж 300. Заказ 1.