

The Photoluminescence Properties of CuInS₂ and AgInS₂ Nanocrystals Synthesized in Aqueous Solutions

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The results of investigations of the AgInS₂ and CuInS₂ nanocrystals (NCs) by the photoluminescence (PL), PL excitation (PLE), optical absorption, Raman scattering and X-ray diffraction (XRD) methods are presented. The NCs were synthesized under stoichiometric conditions in aqueous solutions in the presence of aliphatic mercaptoacids and transferred in polymer films of gelatin. The XRD patterns and Raman spectra indicated formation of the AgInS₂ and CuInS₂ NCs of chalcopyrite phase mainly of the average size of about 4 and 2 nm, respectively. The PL spectra of the NCs showed intense defect-related band being much broader for the AgInS₂ crystallites. The PLE spectra demonstrated strong dependence on the emission position in the PL spectrum. The low-temperature PL study showed that the PL band of the AgInS₂ NCs consisted of two components originated from the ensembles of the NCs of different crystal structure presumably of the chalcopyrite and cubic phases.

Introduction

The CuInS₂ and AgInS₂ are the low-toxic I-III-VI semiconductor materials with direct band gap and high absorption coefficient in the visible and near-IR regions. The CuInS₂ owing to the excellent energy matching between its band gap (1.5 eV) and the solar spectrum for decades has been considered as a promising candidate for application in thin film solar cells (1). Development of the methods for synthesis of I-III-VI nanocrystals (NCs) (2) opened new prospects for application of these materials in the fields of photovoltaic (3-5), optoelectronics (6-9) and biomedical imaging (10). In the last case, the interest was motivated by the searching of highly luminescent materials composed of the elements that are available in large quantities and with reduced toxicity. In fact, a number of successful applications of the CuInS₂ and AgInS₂ NCs for both in vitro and in vivo imaging have been demonstrated (11-14).

As compared with the organic dyes, the I-III-VI NCs have comparable or higher quantum yield, much larger photo-stability and absorption cross section. Specifically, the quantum yield of the AgInS₂ and CuInS₂ NCs covered by a ZnS shell can reach 80 % (2) and 60 % (11), respectively. The I-III-VI NCs are also characterized by a broad absorption spectrum and a large Stokes shift of the PL band (11). The broad PL band is usually attributed to radiative transitions via intragap states formed by structural defects

inside or at the surface of the NCs, including the free-to-bound, bound-to-free or bound-to-bound transitions in the donor-acceptor (DA) pairs (15-17). Ternary I-III-VI semiconductors are known to be abundant of intrinsic point defects due to existence of two kinds of differently sized cations. In the CuInS_2 and AgInS_2 NCs, the defects participating in the radiative transitions include sulfur vacancies, silver (copper) interstitials and indium substituted at a silver (copper) site acting as donors, while silver (copper) vacancies, sulfur interstitials and silver (copper) substituted at an indium site acting as acceptors (16, 18). The particular type of the defects would depend on the stoichiometry of the NCs, i.e. on Cu (Ag) - rich or In-rich phases. The latter affects also the band gap of the material. Specifically, the chalcopyrite and orthorhombic phases of the AgInS_2 show at room temperature a direct band gap of about 1.87 and 1.98 eV (19), respectively, and AgIn_5S_8 compound with the cubic spinel structure has a direct band gap of about 1.78 eV at 295 K (20). By changing the [Cu] : [In] and [Ag] : [In] molar ratios as well as the reaction temperature the I-III-VI NCs of certain crystal structure can be obtained (2, 21, 22). However, formation of the I-III-VI NCs of different crystal phases at specific conditions of synthesis has also been reported (22).

Despite the fact that different strategies have been developed for the synthesis of I-III-VI NCs (2), it still remains a challenge to develop a facile, general and inexpensive method for the preparation of I-III-VI NCs with controllable luminescence spectrum. This is particularly relevant for the synthesis in organic media that allow producing water-dispersible NCs required for biological applications. Moreover, the aqueous synthetic routes are generally more environment-friendly, low-cost and biocompatible.

Herein, we present the results of the investigations of the PL, optical and structural properties of the CuInS_2 and AgInS_2 NCs synthesized under stoichiometric conditions in aqueous media in the presence of mercaptoacetic acid. The peculiarities of the PL characteristics of two types of the NCs embedded in polymer film of gelatin are studied.

Experimental details

The CuInS_2 and AgInS_2 NCs were synthesized at room temperature by interaction between a mixture of mercaptoacetate complexes of In^{III} and Cu^{I} (Ag^{I}) with Na_2S in water under stoichiometric conditions (an [Cu]:[In]:[S] and [Ag]:[In]:[S] molar ratios of 1:1:2). In a typical procedure, 0.1 mL stock 0.1 M solution of CuNO_3 (AgNO_3), 0.15 mL stock 1.0 M solution of NaOH and 0.15 mL stock 1.0 M solution of MAA were added to 8.3 mL distilled water at vigorous stirring. Then, 0.1 mL stock 0.1 M solution of InCl_3 and 0.2 mL of freshly prepared stock 1.0 M solution of Na_2S were added to the homogenized mixture at vigorous stirring. To produce the composite polymer films 1 wt.% gelatin was introduced into the NC solutions. The resulting viscous solutions (2.5 mL) were dropcasted onto 2.0 cm^2 glass plates and left for natural drying in the dark at room temperature.

X-ray diffraction (XRD) study was realized using X-ray powder diffractometer ARL X'TRA with the $\text{Cu } K\alpha_{1,2}$ radiation. The micro-Raman spectra were excited with a line of 325 nm of a He-Cd laser and collected in a backscattering configuration by a triple Raman spectrometer T-64000 Horiba Jobin-Yvon with a resolution about 0.15 cm^{-1} . The PL and PL excitation (PLE) spectra were studied at 77 and 300 K under excitation by a light of 410 nm LED, 470 nm LED and a halogen-lamp passed through a grating monochromator.

Results and discussion

The XRD patterns of the NCs embedded in the films of gelatin showed an intense diffraction peak caused by an amorphous phase of gelatin matrix and no signals from the NCs apparently due to low concentration of the NCs in polymer (less than 1 % w/v). Therefore, dried NCs were produced for structural investigations. An aqueous solution of colloidal NCs was heated up to 200 °C and kept for 2 hours up to complete evaporation of the solvent.

Figure 1 shows the XRD patterns of dried CuInS_2 and AgInS_2 NCs. Both patterns show the same intense sharp peaks caused by cubic NaCl phase emerged from pristine colloidal solution upon drying and the broad peaks of much lower intensity related to the NCs. The major diffraction peaks at about $2\theta = 27.9^\circ$, 46.4° and 54.65° in the XRD pattern of dried CuInS_2 NCs (Fig.1, curve 1) as well as the peaks at about $2\theta = 27^\circ$, 45° and 53° in the XRD pattern of dried AgInS_2 NCs (Fig.1, curve 2) can be indexed to the (112), (024)/(220) and (116)/(132) reflections, respectively, of the chalcopyrite structure. The XRD peaks of the CuInS_2 NCs matched well with chalcopyrite phase (JCPDS 00-047-1372), while those of the AgInS_2 NCs did not (JCPDS 00-025-1330). Specifically, the peak at about $2\theta = 27^\circ$ is very close to the reflection from both the {112} planes of chalcopyrite AgInS_2 and {311} planes of cubic zinc blend AgIn_5S_8 phase, and the peak at about $2\theta = 53^\circ$ is close to the reflections from the {132} planes of chalcopyrite AgInS_2 and {620} planes of cubic AgIn_5S_8 phase (JCPDS 00-025-1329). This can be the evidence of coexistence of the NCs of both chalcopyrite AgInS_2 and cubic AgIn_5S_8 phases. The average size of the I-III-VI crystallites evaluated from the full width at a half maximum (FWHM) of (112) diffraction peak using the Scherrer equation is about 2 nm for the CuInS_2 NCs and about 4 nm for the AgInS_2 NCs.

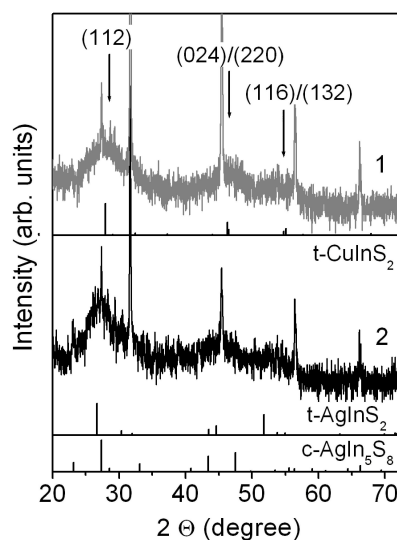


Figure 1. X-ray diffraction patterns of dried CuInS_2 (curve 1) and AgInS_2 (curve 2) NCs.

The Raman spectra of both dried NCs and the NCs embedded in gelatin film were studied. However, the Raman spectra of the NCs embedded in gelatin were not recorded apparently due to intense PL from the NCs passivated by MAA and functional groups of gelatin. The Raman spectra of dried AgInS_2 and CuInS_2 NCs presented in Fig. 2 contain the peaks that can be assigned to the chalcopyrite structure. Typically, in the Raman spectra of chalcopyrite I-III-VI compounds, the A_1 mode caused by the vibration of the

anion sublattice is the most intensive and is considered as the characteristic mode (23). In the Raman spectra of bulk chalcopyrite CuInS_2 crystals, the A_1 mode is experimentally observed at about 292 cm^{-1} , which is close to the estimated value of 294 cm^{-1} (23, 24). In turn, for bulk chalcopyrite AgInS_2 crystals the estimated vibrational frequency of the A_1 mode is 282 cm^{-1} (24). Therefore, the peak at 292.5 cm^{-1} (Fig. 2, curve 1) is ascribed to the A_1 mode of the chalcopyrite CuInS_2 phase, and the peak at about 290 cm^{-1} (Fig. 2, curve 2) is supposed to belong to the A_1 mode of the chalcopyrite AgInS_2 phase. Another less pronounced shoulder peak at about $345\text{--}350\text{ cm}^{-1}$ can be ascribed to the $E_{\text{LO}}^1/B_{2\text{LO}}^1$ modes of the chalcopyrite structure (23, 24).

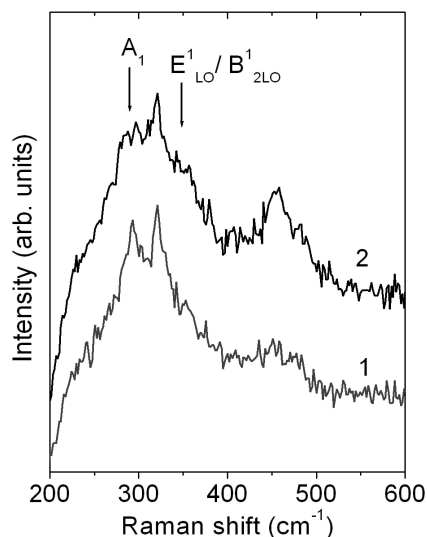


Figure 2. Raman spectra of dried CuInS_2 (curve 1) and AgInS_2 nanocrystals (curve 2), $T=300\text{ K}$, $\lambda_{\text{exc}}=325\text{ nm}$.

It should be noted that the Raman spectrum of the AgInS_2 NCs shows larger FWHM of the peak at about 290 cm^{-1} and larger relative intensity of the peak at about 345 cm^{-1} as compared with those of the CuInS_2 NCs. This allows supposing contribution of some secondary phases to the spectrum. Specifically, the peak at about 290 cm^{-1} is close to the frequency of the F_{2g} mode and the shoulder at about 345 cm^{-1} is close to the A_{1g} mode of cubic AgIn_5S_8 phase (25). Therefore, we can suppose that the Raman spectrum of the AgInS_2 NCs shows the presence of the chalcopyrite AgInS_2 phase with an admixture of secondary, presumably of the cubic AgIn_5S_8 phase. The nature of the intense peaks at about 320 , 450 and 480 cm^{-1} remains unclear. Most likely these peaks are not connected with the NCs and are caused by the presence of some by-products of the synthesis or other secondary phases.

Figure 3 shows the room-temperature optical absorption, PL and PLE spectra of the CuInS_2 and AgInS_2 NCs embedded in gelatin film. The optical absorption spectra show a long tail in the long-wavelength spectral region, but do not show well-defined exciton absorption peak, although a small bend at around 520 nm can be found in the spectrum of the CuInS_2 NCs. A long tail in the absorption spectra of the I-III-VI NCs is usually explained by size/shape inhomogeneity of the NCs and/or by optical transitions via intra band gap states in the NCs. Despite this assignment, the optical band gap of the CuInS_2 and AgInS_2 NCs can be roughly estimated as the onset of the Tauc's plot $(\alpha h\nu)^2$ versus $h\nu$, where α is the absorption coefficient and $h\nu$ is the photon energy. This approach is valid for bulk direct band gap semiconductors (26) but is often used for nanocrystalline

materials too (15, 22). The band onsets at ~ 2.2 eV for the AgInS₂ NCs and at ~ 1.77 eV for the CuInS₂ NCs are larger than the band gap of the bulk chalcopyrite AgInS₂ (1.87 eV) and CuInS₂ (1.5 eV), respectively, apparently due to quantum confinement effect.

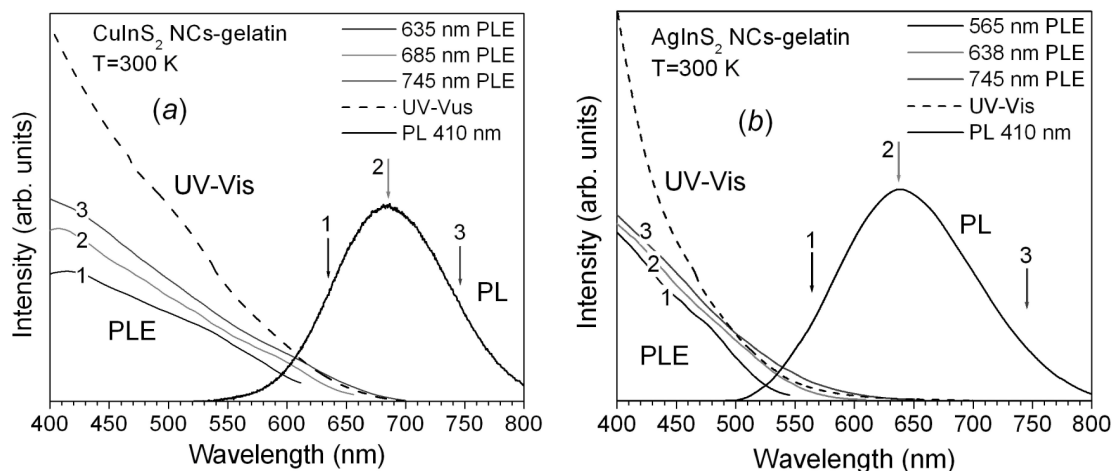


Figure 3. Room-temperature optical absorption (UV-Vis), PL and PLE spectra recorded at different wavelengths in the PL spectrum (marked by arrows) of the CuInS₂ (a) and AgInS₂ (b) NCs embedded in gelatin. The PL spectra are recorded under excitation of a light of 410 nm LED.

In the PL spectra, wide band with maximum at about 1.81 eV (~ 685 nm) for the CuInS₂ NCs (Fig. 3a) and 1.94 eV (~ 638 nm) for the AgInS₂ NCs (Fig. 3b) is observed. The PL band approximated by a single Gaussian function shows the FWHM of about 0.39 eV (~ 140 nm) for the AgInS₂ NCs and 0.25 eV (~ 110 nm) for the CuInS₂ NCs. The accurate determination of the Stokes shift magnitude, known as a difference between the emission and absorption peaks, might be difficult because of the absence of distinct exciton-related feature in the absorption spectrum. For the CuInS₂ NCs the energy difference between the bend at around 2.38 eV in the absorption spectrum and the PL peak position is ~ 0.58 eV. For the AgInS₂ NCs the determination of the Stokes shift from the PL and absorption spectra seems to be impossible.

In the PLE spectra of both the AgInS₂ and CuInS₂ NCs recorded at different emission positions, the absorption edge shifts to longer wavelengths as the wavelength of the emission light increases. This is valid for the emission wavelengths from the entire PL spectrum. Besides, in the PL excitation spectrum of the AgInS₂ NCs recorded at the high-energy wing of the PL band, an obvious hump at about 470-480 nm appears.

The large FWHM of the PL band of both types of the NCs and large Stokes shift testify to defect-related nature of the PL band. The large FWHM of the PL band can be caused by several factors, alone or in combination with each other. Firstly, it can originate from the strong electron-phonon interaction. Specifically, the relatively large Huang-Rhys factor of $S=23$ have been reported for the AgInS₂ NCs (16). The simulation of the PL band in the AgInS₂ NCs has shown that the zero-phonon line is positioned on the high-energy tail of the PL spectrum and almost the entire PL spectrum is identified as phonon sidebands (16). This factor seems to be the main for determining the large FWHM of the defect-related PL band in the I-III-VI NCs. Secondly, the inhomogeneity of the NCs in size can produce a scattering of energies for optical transitions. In fact, a constant shifting of the absorption edge in the PLE spectra to the longer wavelengths, as the emission wavelength within the PL band increases, indicates that a size distribution of

the NCs contributes also to the stretched tail in the optical absorption spectrum and FWHM of the PL band. Thirdly, the large FWHM of the PL band can be caused by contribution of two or more defect-related PL bands of different nature.

To study the PL characteristics of the NCs in more detail, the PL and PLE spectra were recorded at liquid nitrogen temperature (Fig. 4). As the polymer films are cooled from 300 K to 77 K, the PL intensity increases in 3-5 times and the PL peak position shifts to shorter wavelengths. The blue shift is of about 10 nm for the CuInS_2 NCs and is in the range of 30-40 nm for the AgInS_2 NCs. Moreover, the PL band of the AgInS_2 NCs becomes broader and clearly asymmetric (Fig. 4b). It can be well fitted with two Gaussians with maxima at about 560 nm and 635 nm, the FWHM of each of the components being of about 0.33 eV.

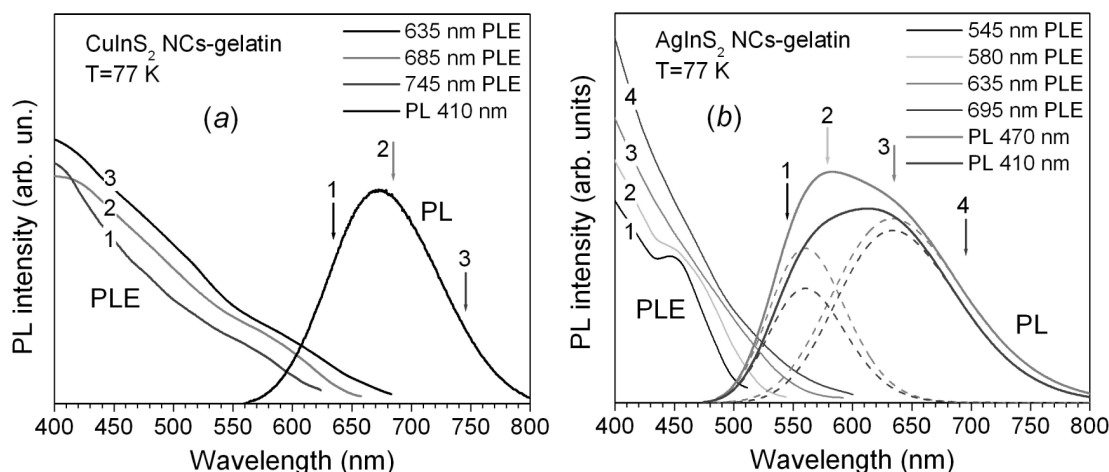


Figure 4. Low-temperature PL and PLE spectra recorded at different wavelengths in the PL spectrum (marked by arrows) of the CuInS_2 (a) and AgInS_2 (b) NCs embedded in gelatin. The PL spectra are excited by a light of 410 nm LED and 470 nm LED, their decomposition with two Gaussians are shown by dashed lines.

The PLE spectra of the CuInS_2 NCs recorded at different emission wavelengths within the PL band show the weak bend and stretched absorption edge, both shifting to longer wavelengths as the emission wavelength increases within the PL band (Fig. 4a). In contrast, the PLE spectra of the AgInS_2 NCs recorded at the high-energy and low-energy wings of the PL band show different shape. The PLE spectrum of the high-energy PL component shows a distinct well-defined maximum at about 450 nm (~ 2.75 eV), while those of the low-energy PL component does not show (Fig. 4b). When the emission position for monitoring the PLE spectrum is shifted to longer wavelengths, the absorption edge also shifts to longer wavelengths. This is observed in the PLE spectra of both PL components of the AgInS_2 NCs, the absorption edge in the PLE spectra of the low-energy PL component being shifted to longer wavelengths as compared with that of the high-energy PL band. The presence of well-defined absorption peak in the PLE spectra allows estimating the Stokes shift magnitude for the high-energy PL component of the AgInS_2 NCs of about 0.5 eV. The Stokes shift magnitude for the low-energy PL component is supposed to be larger.

It should be noted that spectral position of the PL band maximum of the CuInS_2 NCs is nearly independent on the excitation wavelength, while that of the AgInS_2 NCs varies within the range of 580-630 nm. The latter is originated mainly from the change of

contribution of two PL components in the spectrum as the excitation wavelength is changed (Fig. 4b). Specifically, when a light of 470 nm, which coincides with the PLE maximum is used for excitation, the PL peak position shifts to 580 nm, while a light of 410 nm excites stronger the low-energy PL component and produces a shifting of the PL peak position to 610 nm.

The obtained results of the low-temperature PL investigations clearly indicate that defect-related PL band of the AgInS_2 NCs has a complex structure and is composed at least of two components. This seems to be the main reason of a much larger FWHM of the room-temperature PL band of the AgInS_2 NCs as compared with that of the CuInS_2 NCs. The different PL excitation spectra of two PL components imply that the defects responsible for each of the components are located in different ensembles of the NCs. The XRD data together with the results of Raman spectra allow supposing that these two ensembles of the NCs differ in crystal structure, in particular in crystal phase. It can be suggested that the high-energy PL component is caused by the defects in the NCs of cubic AgIn_5S_8 phase, while the low-energy PL component is related to the defects in the chalcopyrite AgInS_2 NCs. In fact, the increasing of In content in the AgInS_2 NCs has been reported to result in the shifting of both the absorption edge and PL spectrum to shorter wavelengths (9, 21, 22). The optical absorption spectra of the cubic AgIn_5S_8 NCs often show a clear hump in contrast to that of the chalcopyrite AgInS_2 NCs. The reported Stokes shift magnitude for the cubic AgIn_5S_8 NCs of about 0.66 eV (22) is much smaller than the shift values 0.8–1.0 eV estimated for the chalcopyrite AgInS_2 NCs (27).

The NCs of cubic In-rich phase can nucleate under stoichiometric conditions of synthesis if some secondary Ag-related phase is formed. For instance, simultaneous formation of the inclusions of cubic CuIn_5S_8 phase and secondary Cu_xS phases in the CuInS_2 films produced by different methods under $[\text{Cu}]:[\text{In}]$ ration of 0.8–1.0 has been reported (28, 29) and ascribed to disorder effects in the CuInS_2 lattice. Similarly, formation of some amount of the inclusions of AgIn_5S_8 cubic phase has been mentioned for the AgInS_2 films synthesized via the sulfurization of Ag–In metal precursors under $[\text{Ag}]:[\text{In}]$ ratios below 0.79 (30). In our case a sideway process of AgCl phase formation during the synthesis can decrease an $[\text{Ag}]:[\text{In}]$ ratio in the NCs and promote the formation of cubic AgIn_5S_8 crystallites.

Conclusion

The peculiarities of the PL properties of the AgInS_2 and CuInS_2 NCs synthesized in aqueous solutions have been investigated. The XRD study proved the formation of the crystallites of preferred chalcopyrite phase with the average size of about 2 nm for the CuInS_2 NCs and 4 nm for the AgInS_2 NCs. The NCs embedded in polymer films of gelatin show an intense PL band ascribed to radiative transitions via the levels of intrinsic defects in the NCs. The PL band is characterized by the large FWHM (~100–150 nm) and large Stokes shift of several hundreds meV. The PL spectrum of the AgInS_2 NCs is shown to be caused by contribution of two PL bands. It is assumed that these PL bands are originated from the defects located in the ensembles of the NCs of different crystal structure. It is supposed that the crystallites of the chalcopyrite AgInS_2 and cubic AgIn_5S_8 phases are responsible for complex structure of the PL band.

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