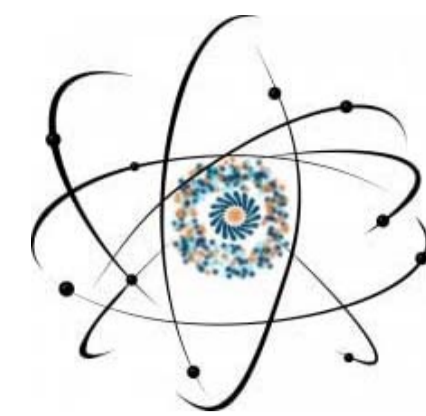


Glutathione-capped quaternary Ag–(In,Ga)–S quantum dots obtained by colloidal synthesis in aqueous solutions



B.V. Lopushanska¹, Yu.M. Azhniuk^{1,2}, V.V. Lopushansky²,

I.P. Studenyak¹, D.R.T. Zahn³

¹ Uzhhorod National University, Pidhirna Str. 46, Uzhhorod, 88000, Ukraine, lopushanska5@gmail.com

² Institute of Electron Physics. Ukr. Nat. Acad. Sci., Universytetska Str. 21, Uzhhorod, 88000, Ukraine

³ Semiconductor Physics, Chemnitz University of Technology, Chemnitz D-09107, Germany



INTRODUCTION

Research interest towards I–III–VI colloidal semiconductor quantum dots (QDs) is caused by their non-toxicity and the possibilities of size variation of their bandgap in a broad range, high luminescence efficiency, high photocatalytic activity, and possible applications in biology and medicine as well as in light sources and photovoltaic elements [1,2]. Much less studied are gallium containing Ag–(In,Ga)–S QDs [3,4]. To our knowledge, no studies of size-selected Ag–(In,Ga)–S QDs have been presented so far.

Here we report on the synthesis and optical characterisation of size-selected quaternary non-stoichiometric Ag–(In,Ga)–S QDs obtained at mild conditions in the presence of glutathione (GSH) from aqueous solutions with different [In]:[Ga] molar ratios in the reaction mixture.

Ag–(In,Ga)–S QUANTUM DOT FABRICATION

Ag–(In,Ga)–S QDs were obtained following the method by Raevskaya et al. for Ag–In–S [1] with some modifications.

aqueous solutions AgNO₃ + GSH + NH₄OH + InCl₃ + GaCl₃ + Na₂S (in desired proportions)

at intense stirring

↓ aging for 30 min at 90–95 °C ↓

luminescent Ag–(In,Ga)–S quantum dots



Size-selective fractioning: precipitation in the presence of isopropanol by centrifugation (4000 rpm, 5 min)

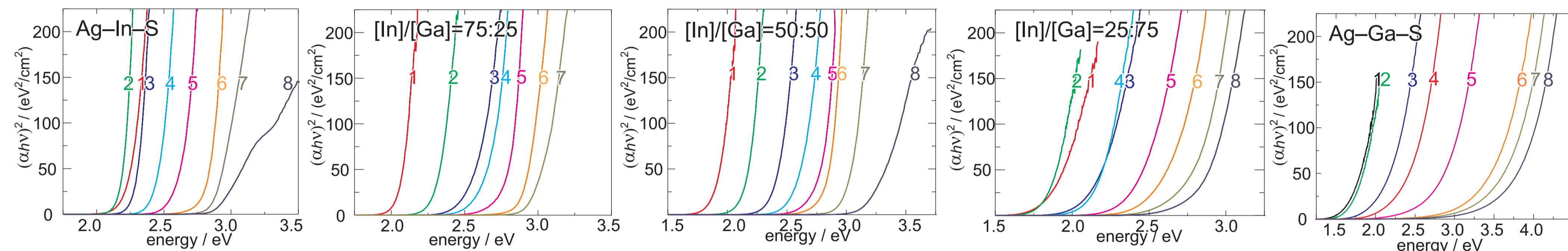
Size-fractionated Ag–(In,Ga)–S QDs, [Ag]:[In+Ga]:[S]=1:4:5, [In]:[Ga]=50:50

OPTICAL CHARACTERISATION

Optical absorption measurements: Cary 50 spectrophotometer (Varian) with a full spectrum Xe pulse lamp single source and dual Si diode detectors.

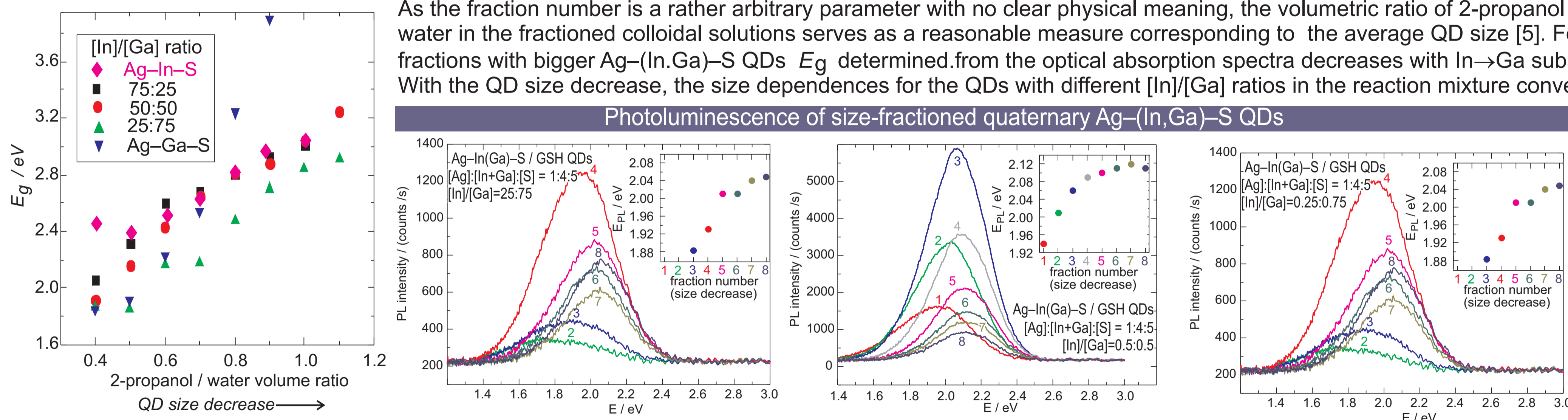
Photoluminescence (PL) measurements: Black Comet CXR-SR spectrometer (StellarNet) with excitation by a diode (390 nm).

Optical absorption of size-fractionated Ag–(In,Ga)–S QDs prepared with different [In]/[Ga] ratios in the reaction mixture



As the fraction number is a rather arbitrary parameter with no clear physical meaning, the volumetric ratio of 2-propanol and water in the fractionated colloidal solutions serves as a reasonable measure corresponding to the average QD size [5]. For the fractions with bigger Ag–(In,Ga)–S QDs E_g determined from the optical absorption spectra decreases with In→Ga substitution. With the QD size decrease, the size dependences for the QDs with different [In]/[Ga] ratios in the reaction mixture converge.

Photoluminescence of size-fractionated quaternary Ag–(In,Ga)–S QDs



CONCLUSIONS

- 1 Luminescent non-stoichiometric Ag–(In,Ga)–S QDs capped with glutathione were synthesised from aqueous solutions at different [In]/[Ga] molar ratios in the reaction mixture.
- 2 Fractioning of the solutions obtained by repeated centrifuging with 2-propanol enabled size-selected Ag–(In,Ga)–S QDs to be obtained.
- 3 For all size-selected series of Ag–(In,Ga)–S QDs with different [In]/[Ga] ratios in the reaction mixture size-dependent shift of the absorption edge was clearly observed.
- 4 For the lower fractions (bigger Ag–(In,Ga)–S QDs) the band gap determined from the optical absorption spectra decreases with In→Ga substitution. With the QD size decrease, the size dependences for the QDs with different [In]/[Ga] ratios converge.
- 5 Increase of Ga content in the QDs leads to a decrease of the PL intensity. The PL maximum energy for all the QD series steadily (although slightly) increases with decreasing QD size. The Stokes shift value also increases with decreasing QD size what is typical for the QDs of this family.
- 6 The optical properties of the QDs in the colloidal solutions remain practically unchanged after 3-month storage at room temperature.

REFERENCES

- [1]. A. Raevskaya, V. Lesnyak, D. Haubold, V. Dzhanan, O. Stroyuk, N. Gaponik, D.R.T. Zahn, A. Eychmuller, J. Phys. Chem. C 2017, 121, 9032–9042.
- [2]. O. Stroyuk, A. Raevskaya, F. Spranger, O. Selyshchev, V. Dzhanan, S. Schulze, D.R.T. Zahn, A. Eychmuller, J. Phys. Chem. C 2018, 122, 13648–13658.
- [3]. N. Liang, Q. He, S. Huang, M. Wang, W. Chen, M. Xu, Y. Yuan, J. Zai, N. Fang, X. Qian, CrystEngComm 2014, 16, 10123–10130.
- [4]. T. Bai, X. Wang, Y. Dong, S. Xing, Z. Shi, S. Feng, Inorg. Chem. 2020, 59, 5975–5982.
- [5]. B.V. Lopushanska, Y. M. Azhniuk, D. Solonenko, V. V. Lopushansky, I.P. Studenyak, D. R. T. Zahn, Molecular Cryst. Liquid Cryst. 2021, 717, 98–108.

ACKNOWLEDGEMENTS

The authors are grateful to A.I. Pogodin, Ya.I. Lopushanska, and O.P. Kokhan for their assistance. Yu.M. Azhniuk is grateful to TU Chemnitz for the funding of his research stay at the university.

Contact: lopushanska5@gmail.com (Bohdana Lopushanska)