Review of the Dissertation Thesis of Mgr. Dianna Himics

„Physico-chemical and optical properties of Er^{3+}-doped and Er^{3+}/Yb^{3+}-, Er^{3+}/Ho^{3+}-co-doped chalcogenide glasses"

Submitted thesis of Mgr. Dianna Himics contains results of her work during the doctoral studies at the Faculty of Chemical Technology, University of Pardubice. The dissertation consists of 89 pages including the references and the list of authors publications related to the thesis subject. It is subdivided into three chapters supplemented by the Abstract, Conclusions, list of figures and tables, and the list of abbreviations and symbols used. The dissertation is written in English and has a quite good graphical arrangement. The goals of the dissertation are not stated explicitly. The abstract gives the summary of the work and of obtained results. The core of the dissertation is given in chapter III. (Results and discussion) where are presented and discussed results obtained for the two investigated glass systems - GeGaSbS: Er/Yb and GeGaS: Er/Ho.

The first chapter (Theoretical background, pp. 14-43) provides basic information on the structure, thermal and optical properties of chalcogenide glasses. Special attention is devoted to absorption and luminescence. Doping with rare-earth ions (particularly Er^{3+}, Ho^{3+} and Yb^{3+}) and possible up-conversion processes mediated by RE^{3+} ions are explained. Various up-conversion processes are discussed both for single RE-doped and RE co-doped glasses. The Judd-Ofelt theory for spectroscopic analysis from measured transmission spectra of RE-doped chalcogenide glasses has been presented in a reasonable detail. The experimental techniques used for the preparation of investigated glasses as well as their characterization are presented in Chapter II (Experimental method used for room temperature measurements, pp. 44-50). The author was able to exploit a number of sophisticated techniques including XRD, EDS, DSC, Raman scattering and spectroscopic ellipsometry that enabled a quite complex physico-chemical characterization of investigated glasses. The last chapter (Results and discussion, pp. 51-74) is divided into two parts according to the investigated glass systems. Obtained results for the GeGaSbS: Er/Yb glasses are presented and discussed in part 3.1, while similar analysis for the system GeGaS: Er/Ho is given in part 3.2. The physico-chemical characterization of prepared samples has been performed with emphasis on transmission and *4f-4f* luminescence properties. Prepared glasses were investigated in detail by the room-temperature transmission spectroscopy in a broad spectral range (UV-Vis-NIR) and room-temperature photoluminescence spectroscopy in the spectral range 500-1700 nm. In addition, the time-resolved luminescence of doped-in Er^{3+} ions was measured. Er-doped and Er/Yb co-doped GeGaSbS systems were investigated with emphasis on the influence of Yb sensitization on up-conversion and also on the main Er^{3+} luminescence band at 1530 nm. Judd-Ofelt analysis for Er doped quaternary system has been performed. Similar analysis of GeGaS system doped with Er and co-doped with Er/Ho has been given in part 3.2. The time resolved photoluminescence has been used in case of the GeGaS glass that enabled the determination of the lifetime for $^4I_{13/2}$ manifold both for single doped Er and Er/Ho co-doping. The Judd-Ofelt analysis has been performed in case of GeGaS glass for both Er^{3+} and Ho^{3+} and obtained parameters were used for the estimation of $Er^{3+} \rightarrow Ho^{3+}$ energy transfer parameter. Photoluminescence was investigated under the excitation by 980 nm and the role of Er^{3+} ions as sensitizers for Ho^{3+} related emission and up-conversion has been investigated and discussed. The study of Er/Ho co-doping under the 980 nm excitation is interesting in view of the fact that Er and Ho do not have resonant low laying energy manifolds and only Er^{3+} ions interact directly with the used excitation wavelength. I appreciate that some results have already been published – three papers in impacted journals and a number of conference contributions.

Minor comments to Chapter I. and the Thesis in general.

- Smaller fonts as compared to ordinary text should have been used for Figure and Table captions and also the line spacing should have been smaller, to facilitate the reading.
- The thesis contains a number of misprints and grammatical mistakes. Some misprints change the meaning of the sentence(see for example p. 21: *.......while at longer wavelengths it is limited by multiphoton absorption; The glass transition at shorter wavelengths is limited ....;* p. 27: *The optical transitions typical of rare earth spectra are attributed to infra-4f ....;* p. 39: *Infra-$4f^N$ electronic transitions are called......).*
- Expresion (5) on p. 22 simply gives the formula for the conversion of energy (units in eV) to corresponding wavelength λ (units in μm), and it can be used, for example, also for conversion of the band gap energy.
- The statement on p. 22: „*The optical band gap E_g is usually estimated as the photon energy corresponding to an absorption coefficient α equal to 10 cm^{-1}.*" is not generally true and should have been correlated with the shape of the absorption coefficient $\alpha(\lambda)$ presented in Fig. 4 – particularly with the right diagram in Fig. 4.
- The statement on p. 22: „*The absorption coefficient α is related to the material's thickness d according to.......expression (6)*" is confusing. The absorption coefficient as a material parameter does not depend on the dimension of the sample. The phrase should read for example: "*The absorption coefficient could be expressed as a function of measured intensity of transmitted and incident radiation (I and I_0, respectively) and the width d of measured glass sample.*"
- p. 23 Transition from expression (7) to expression (8) is not explained and it is not straightforward. Comment of the type: *Equation (8) takes into account the multiple reflections and expresses the absorption coefficient as a function of measured transmittance $T(\lambda)$ and estimated reflectance $R(\lambda)$. Reflectance $R(\lambda)$ could be estimated for example by using formula (7).";* should have been added.
- p. 29 The Stark levels splitting due the influence of the surrounding crystal field is demonstrated in Fig. 6 (the schematic energy level diagram). In reality the splitting is much smaller than the energy distance between adjacent manifolds so that the Stark levels of respective manifolds do not overlap. In ref. [49] is given the energy spread of respective energy levels, so that the schematic picture in [49] is not confusing. However, the energy scale for respective levels is missing in Fig. 6 in the thesis.

For the discussion during the defence I have several points to be clarified.

- It would be useful to compare the properties of (undoped) base glass systems with doped ones. It specially concerns transmission spectra. Were the respective base glasses prepared?
- It follows from data presented in Fig. 13 that the fundamental absorption edge of the GeGaSbS glass host exhibits a considerable red shift with increasing concentration of Yb. Do you have an explanation of this phenomenon?

- Data presented in Table 1, for $Ge_{25}Ga_{9.5}Sb_{0.5}S_{65}$:Er/Yb samples, show that germanium (Ge) and gallium (Ga) concentrations exhibit a bigger span of values with increasing Yb concentration, compared to concentration of sulphur (S), and especially in contrast to the GeGaS system doped with Er/Ho (Table 6). Could this behaviour of quaternary system be interconnected with the shift of the fundamental absorption edge with increasing Yb co-doping? How the system would behave if the Yb addition would be compensated by addition of stoichiometric amount of sulphur? What was the reproducibility of samples preparation?

- It follows from data presented in Fig. 17 that "*the PL emission intensity decreases with increasing Yb^{3+} content*". Could this behaviour be, at least partially, assigned to the decreasing number of Er^{3+} ions related to different valence state of the system with increasing addition of Yb in the form of metal?

- The statement on p. 68 (in relation to ref. [100]): "*This mechanism has been proven by the Ho^{3+}: $^5I_6 \rightarrow {}^5I_8$ ($\lambda \sim 1.2\ \mu m$) emission spectra in GeGaS:Er^{3+}, GeGaS:Ho^{3+} and GeGaS:Er^{3+}/Ho^{3+} glasses at pumping wavelength of 980 nm presented in Fig. 22.*", does not apply to GeGaS:Er and GaGaS:Ho samples – but only to GeGaS:Er/Ho samples. The $^5I_6$ level of Ho^{3+} lies about 1290 cm^{-1} below the $^4I_{11/2}$ level of Er^{3+}. The question arises how efficiently could this energy difference (1290 cm^{-1}) be dissipated by GeGaS network.

- The expression at the top of page 70: "*$I = Ae^{-t/\tau} + I_0$, where I and I_0 are the luminescence intensities at time t, and A is fitting constants, τ is the lifetime*". - is not appropriate and a more common expression: $I(t) = I_0 \times \exp(-t/\tau)$, where I_0 is the PL intensity at t=0 and I(t) is the PL intensity at time t, is recommended where only the lifetime τ is fitted.

- p. 71; In reference to Fig. 25 – did you try to measure the PL also in the spectral range 750 – 850 nm? If yes – did you find some signal at about 760 and 810 nm? (compare with similar experiment in ref [100]).

The submitted Dissertation Thesis documents that the author is capable of research work leading to new results that could be published in international impacted journals. She showed good orientation in the use and interpretation of various complementary experimental techniques to characterize prepared glass samples.

I recommend the Disseratation Thesis of Mgr. Dianna Himics for the defence.

Prague, August 12., 2019

RNDr. Jiří Zavadil, CSc.

Oponentský posudek disertační práce Mgr. Dianny Himics.

Název práce: Physico-chemical and optical properties of Er^{3+}-doped and Er^{3+}/Yb^{3+}-, Er^{3+}/Ho^{3+}-co-doped chalcogenide glasses.

Školitel: Prof. Ing. Tomáš Wagner, DrSc.

V předložené práci je zkoumána struktura, fyzikální a spektroskopické vlastnosti objemových vzorků chalkogenidových skel o složení Ga-Ge-Sb-S dopovaných prvky vzácných zemin, jako Er^{3+}, Yb^{3+} a Ho^{3+}. Téma patří do tradiční oblasti výzkumu na pracovišti disertantky, což samo zaručuje dobrou vědeckou i formální úroveň posuzované disertace. Vcelku téma disertace považuji za vědecky zajímavé a to zejména s ohledem na praktický význam těchto materiálů v současnosti i v budoucnosti v řadě aplikací (solární články, infračervená optika aj.). Podle mého názoru téma práce zapadá do aktuálních světových trendů v oblasti materiálového výzkumu.

Samotná disertační práce je zpracována přehledně. Je rozdělena do tří hlavních kapitol. První kapitola obsahuje základní informace o struktuře a vlastnostech chalkogenidových skel a je v ní také rozebrána využitá technika vyvinutá Juddem a Ofeltem. V další kapitole jsou charakterizovány techniky využité pro studium vlastností připravených vzorků, poslední kapitola je věnována popisu výsledků měření a jejich interpretaci. Autorka prokazuje dobré znalosti jak materiálové stránky řešené problematiky, tak i související problematiky chemické. Rovněž popis metod využitých ke studiu struktury těchto skel je výstižný. Tuto část disertace tedy považuji za zcela adekvátní a dobře zpracovanou. Uváděná literatura použitá v disertaci zahrnuje významné zdroje v této mezioborové problematice. V úvodních dvou kapitolách autorka prokazuje dobré znalosti vlastní řešené problematiky disertační práce a je schopna je zasadit do širších souvislostí v rámci oboru studia skelného stavu. Autorka přehledně popisuje podstatu defektů souvisejících s dopováním ve sklech a objasňuje podrobnosti formování jejich optických vlastností a související vliv dopantů. Má dobrý přehled znalostí presentovaných v související literatuře a dovede je aplikovat.

Práce má zřejmý cíl, i když není explicitně v práci definován, ale je zřejmý. Je jím UPCL luminiscence ve studovaných systémech chalkogenidových skel a studium vlivu jednotlivých dopantů vzácných zemin (Er^{3+} Yb^{3+} a Ho^{3+} a jejich kombinací. Disertantce se podařilo pomocí „melt quenching" techniky připravit tepelně stabilní chalkogenidová skla $Ge_{25}Ga_{9.5}Sb_{0.5}S_{65}$ dotovaná Er^{3+}, jakož i Er^{3+}/Yb^{3+} a Er^{3+}/Ho^{3+} kodotovaná skla. Autorka u některých vzorků prokázala intenzivní UCPL luminiscenci s takovými parametry, že by materiál mohl být vhodný pro praktické UCPL aplikace, což je jistě dobrý výsledek. Proto podle mého názoru i výsledková část disertace svou úrovní i rozsahem odpovídá požadavkům na doktorskou disertační práci. I počet publikovaných vědeckých prací a jejich vědeckou úroveň považuji za přijatelnou.

Dotazy:

1. K syntéze vzorků. Není mi úplně jasné, jak byla skutečně realizována procedura „The homogeneous melt was quenched into cold water and the glass was annealed at near glass transition temperature (Tg - 20) for 2 h and then slowly cooled down to room temperature" (str. 46).

2. Jsou vzorky z obr. 11, str. 52 skutečně amorfní? Stejně tak obr. 18, str. 64. Nezkoušela jste elektronovou difrakci pomocí TEM? Rovněž použití termínu „light“ pro Roentgenovo záření není úplně běžné.
3. Str. 54, EDS analýza. Použila jste nějakou kalibraci. Obecně je EDS analýza považována za semikvantitativní a výsledky mohou být zatíženy značnou chybou.

Jako celek hodnotím práci jako kvalitní a dobře přijatelnou z hlediska přiznání titulu PhD. Negativní připomínky k ní nemám. Pozitivně hodnotím i dosavadní publikační aktivitu disertanta, tři publikace v kvalitních mezinárodních časopisech na WOS považuji za publikační aktivitu odpovídající požadavkům na udělení titulu PhD.

Závěrem proto konstatuji, že podle mého názoru Mgr. Dianna Himicz splnila požadavky vyžadované pro udělení titulu PhD příslušnými zákony. Doporučuji proto, aby práce byla k obhajobě přijata a disertantce titul PhD udělen.

V Řeži 27. 8. 2019

Ing. Jan Šubrt, CSc.

Reviewer's opinion of dissertation thesis

Physico-chemical and optical properties of Er^{3+} -doped and Er^{3+}/Yb^{3+} -, Er^{3+}/Ho^{3+} -co-doped chalcogenide glasses

Author: Mgr. Dianna Himics

The handed thesis is mainly focused on the preparation and characterization of $Ge_{25}Ga_{9.5}Sb_{0.5}S_{65}$ glass doped with Er^{3+} atoms or co-doped with Er^{3+}/Yb^{3+} atoms as well as GeGaS glass doped with Er^{3+} atoms or co-doped with Er^{3+}/Ho^{3+}atoms. These glasses are expected to exhibit intensive photoluminescence (PL) or up-conversion photoluminescence (UCPL) when excited mainly by the photons of wavelength 980 nm. Currently, these laser active materials are attractive for advanced optical signal processing technologies. Therefore, they have been very intensively studied, developed and applied as crucial components for photonic devices, such as optical amplifiers and sensors.

The theoretical part presents an appropriate introduction to the studied topic and gives enough background for the analysis and discussion of the achieved experimental data. The experimental methods and techniques, described in the following part, were selected correctly and were suitable for the preparation of the glass samples and for their structural, thermal and optical characterizations.

Using the selected experimental techniques, the author was able to obtain a significant database of very interesting experimental results especially the optical spectra of the prepared materials. The author analysed and discussed very well the measured data, utilizing the Judd-Ofelt theory, and proposed useful composition-property relations. Including mainly the effects of glass matrix composition, Er^{3+}/Yb^{3+} co-doping and the role of Yb^{3+} as a sensitizer, concentration quenching influence on PL lifetimes, Ho^{3+}/Er^{3+} co-doping and the very positive role of Er^{3+} sensitizer on PL and UCPL of Ho^{3+}.

As a very significant contribution, I consider the discussion and quantification of the energy transfer from Er^{3+} to Ho^{3+} that are very useful for the glass optimization to reach desired PL properties.

The publication activity of the author was good, as the original research results were published in impacted international journals and presented at international conferences. Because the scientific level of the thesis is high, its research output brings new results and knowledge that are interesting for the international scientific community that specializes in this topic. The text is written in correct English and there are no significant mistakes.

Therefore, I recommend this thesis to be defended by Mgr. Dianna Himics.

For more detailed explanation I have the following questions:

1. How could a glass matrix prevent the concentration quenching?
2. Could you explain the main difference between chalcogenide, chalcohalide and oxychalcogenide glass matrices?
3. Could you show some examples of the devices, an amplifier and a sensor, based on your glass material?

Prague 6. 9. 2019

Associated Professor Martin Míka