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# Ga-Ge-Sb-S: $Er^{3+}$ Amorphous Chalcogenides: Photoluminescence and Photon Up-conversion

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## Abstract

We report on the compositional tuning in $(Ge_{25}Ga_{10-x}Sb_xS_{65})_{99.5}Er_{0.5}$ amorphous chalcogenides ($x$ = 0.5, 2.5 and 5.0 at%) to achieve the intense photon up-conversion emission starting from green spectral region as well as Stokes emission in near- ($\lambda \approx 1.5$ μm) and mid-infrared ($\lambda \approx 2.7$ μm) spectral region. Thermal stability and glass-forming ability were found to increase with increasing antimony content but the photon up-conversion emission in green spectral region exhibits an opposite trend because of the red shift in absorption edge. The spectroscopic properties of $Er^{3+}$ ions in Ga-Ge-Sb-S glassy host matrix were studied on the basis of Judd-Ofelt theory. The calculated spectroscopic quality factor $\Omega_4/\Omega_6$ is approximately 4 higher value than in commercial YAG: $Er^{3+}$ lasers. Emission cross-section $\sigma_e(E)$ of $Er^{3+}$: $^4I_{13/2} \rightarrow {}^4I_{15/2}$ ($\lambda \approx 1.5$ μm) was calculated from absorption cross-section $\sigma_a(E)$ on the basis of McCumber theory. The optical gain coefficient $G(E)$ was calculated as function of the relative population of the $Er^{3+}$: $^4I_{13/2}$ and $^4I_{15/2}$ manifolds. The high absolute values of the gain coefficient make studied materials interesting for lasing and light amplification. The photon up-conversion emission seems to be promising for example in lasers, sensors and detectors.

## Introduction and Goals

Amorphous chalcogenides are attractive host materials for doping them with lanthanide ($Ln^{3+}$) ions. The reason can bee seen in their unique properties such as broad transparency from visible to mid-infrared spectral region, low phonon energy, high refractive index, high solubility of $Ln^{3+}$ ions in chalcogenides containing Ga and their relatively easy preparation in form of bulks as well as thin films [1].

The aims of presented work were:
1) to achieve efficient photon up-conversion emission starting from green spectral region
2) to achieve important near- and mid-infrared Stokes emissions.
3) to study thermal and spectroscopic properties of prepared samples.

The pumping laser diodes used in this work operate at wavelegnths of 808, 980 and 1550 nm.
Studied materials are potentially applicable for lasers, sensors and detectors, erbium doped fiber amplifiers (EDFA) and light detection and ranging (LIDAR) [2].

## Experimental Details

The studied samples were synthesized by standard melt-quenching technique from high-purity elements in silica glassy tubes at 970 C for 24 h. The melt was quenched into water and annealed close to glass transition temperature $T_g$ for 3 h.

### CHARACTERIZATION METHODS

**X-ray Diffraction (XRD) analysis**

Confirmation of amorphous state of prepared samples. Bruker AXE D8-Advance, CuKα tube with secondary graphite monochromator.

**Energy Dispersive X-ray (EDX) spectroscopy**

Confirmation of chemical composition of prepared samples. Microprobe as a part of the SEM microscope JSM-5500 LV Jeol, IXRF System, detector GRESHAM Sirius 10.

**Differential Scanning Calorimetry (DSC)**

Study of thermal properties, i.e. glass transition temperature $T_g$ and crystallization temperature $T_c$. Heating rate: 3 K/min, $N_2$ rate: 50 mL/min. TA Instruments Q2000

**UV/Vis/NIR Spectroscopy**

Record of absorption spectra providing the information about the $4f \leftrightarrow 4f^n$ electronic transitions and about the fundamental absorption of glassy host matrix. Spectral range: 300–2500 nm, step: 2 nm. Double beam spectrophotometer Jasco V-570.

**Spectroscopic Ellipsometry (SE)**

Determination of dispersion of the refractive index. Spectral range: 300–2300 nm, step: 20 nm. Data were evaluated using the Cauchy [3] and Sellmeier [4] formula. The roughness of the samples was modelled using the effective medium approximation (EMA) according to Bruggemann [5] with 50 vol% of voids and 50 vol% of chalcogenide material. VASE®, J.A. Woollam Co., Inc.

**Photoluminescence (PL) Spectroscopy**

Recording of emission spectra and measurement of time-dependent luminescence decay to determine the lifetimes τ. Spectral range: 400–5000 nm, Step: 0.5–2 nm. PL spectrophotometer with pumping lasers of $\lambda_{exc}$ = 808, 980, 1550 nm The variety of detectors such as PMT, InSb, InGaAs, HgCdTe, Ge were used. Measurements were performed at room temperature.

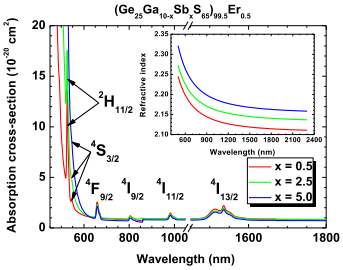


**Fig.1.** Absorption cross-section of the $Er^{3+}$:$^4I_{15/2} \rightarrow {}^{2S+1}L_J$ transitions and spectral dispersion of the refractive index (Figure inset) in $(Ge_{25}Ga_{10-x}Sb_xS_{65})_{99.5}Er_{0.5}$ glasses.

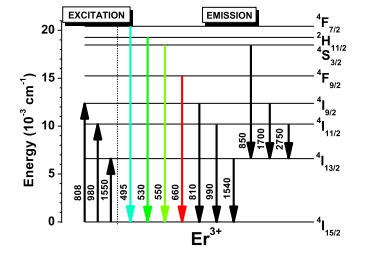


**Fig.2.** Energy level diagram of $Er^{3+}$ ion with observed $4f^n \rightarrow 4f^n$ electronic transitions in $(Ge_{25}Ga_{10-x}Sb_xS_{65})_{99.5}Er_{0.5}$ glasses.

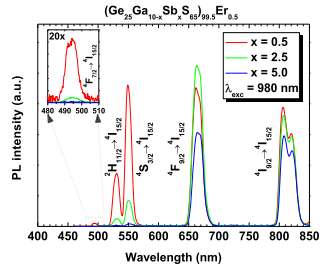


**Fig.3.** Up-conversion spectra of $(Ge_{25}Ga_{10-x}Sb_xS_{65})_{99.5}Er_{0.5}$ glasses at pumping wavelength of $\lambda$ = 980 nm.

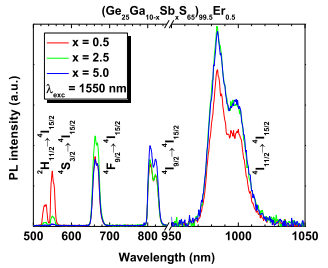


**Fig.4.** Up-conversion spectra of $(Ge_{25}Ga_{10-x}Sb_xS_{65})_{99.5}Er_{0.5}$ glasses at pumping wavelength of $\lambda$ = 1550 nm.

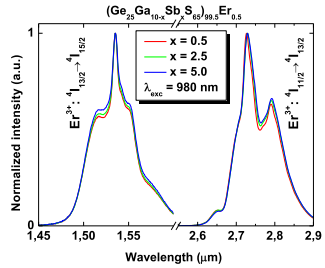


**Fig.5.** Stokes emission spectra of $(Ge_{25}Ga_{10-x}Sb_xS_{65})_{99.5}Er_{0.5}$ glasses at pumping wavelength of $\lambda$ = 980 nm.

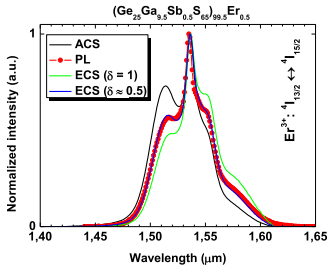


**Fig.6.** Absorption cross-section (ACS) and emission cross-section (ECS) spectra calculated via McCumber theory for the case of homogeneous (δ = 1) and inhomogeneous (δ = 0.5) broadening in $(Ge_{25}Ga_{9.5}Sb_{0.5}S_{65})_{99.5}Er_{0.5}$ glass. The red line (PL) is experimentally measured emission spectrum at pumping wavelength of $\lambda$ = 980 nm.

**Tab.1.** Judd-Ofelt phenomenological parameters $\Omega_2$, $\Omega_4$, $\Omega_6$ and spectroscopic quality factor $\Omega_4/\Omega_6$ of $(Ge_{25}Ga_{10-x}Sb_xS_{65})_{99.5}Er_{0.5}$ glasses.

| $x$ (at %) | $\Omega_2$ ($10^{-20}$ cm$^2$) | $\Omega_4$ ($10^{-20}$ cm$^2$) | $\Omega_6$ ($10^{-20}$ cm$^2$) | $\Omega_4/\Omega_6$ | *rms* ($10^{-20}$ cm$^2$) |
|---|---|---|---|---|---|
| $x$ = 0.5 | 10.16 ± 0.38 | 2.79 ± 0.42 | 1.79 ± 0.15 | 1.57 ± 0.27 | 0.214 |
| $x$ = 2.5 | 6.97 ± 0.29 | 2.11 ± 0.32 | 1.46 ± 0.12 | 1.46 ± 0.25 | 0.166 |
| $x$ = 5.0 | 2.35 ± 11.54 | 1.97 ± 0.53 | 1.48 ± 0.28 | 1.38 ± 0.46 | 0.254 |

**Tab.2.** Mean coordination number (*MCN*), glass transition temperature $T_g$, crystallization temperature $T_c$, melting temperature $T_m$, thermal stability $\Delta T = (T_c - T_m)$ and glass forming ability $H_R = (T_c - T_g)/(T_m - T_c)$ of $(Ge_{25}Ga_{10-x}Sb_xS_{65})_{99.5}Er_{0.5}$ glasses.

| $x$ (at%) | *MCN* | $T_g$ (°C) | $T_c$ (°C) | $T_m$ (°C) | $\Delta T$ (°C) | $H_R$ |
|---|---|---|---|---|---|---|
| $x$ = 0.5 | 2.71 | 417 | 528 | 626 | 111 | 1.14 |
| $x$ = 2.5 | 2.69 | 383 | 508 | 575 | 125 | 1.88 |
| $x$ = 5.0 | 2.67 | 370 | 499 | 555 | 129 | 2.30 |

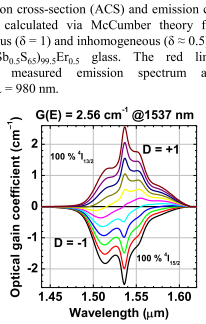


**Fig.7.** Calculated optical gain coefficient $G(E)$ as function of the relative populations of $Er^{3+}$: $^4I_{15/2}$ and $^4I_{13/2}$ manifolds in $(Ge_{25}Ga_{9.5}Sb_{0.5}S_{65})_{99.5}Er_{0.5}$ glass.

## Results & Discussion

Fig.1 shows the absorption cross-section spectra of studied samples with observed $Er^{3+}$ intra-$4f$ electronic transitions (see Fig.2). The absorption edge of samples exhibits a red shift with increasing antimony content. This results in increase of the refractive index as well. This behavior can be attributed to Clausius-Mossotti relation dealing with the atomic polarizability and dielectric function [6].

Observed photon up-conversion emission bands were centered at wavelengths $\lambda \approx$ 495, 530, 550, 660, 810 and 990 nm as show Fig.3 and Fig.4 for pumping wavelengths of 980 and 1550 nm, respectively. The up-conversion emission in the green spectral range is strongly affected by antimony content due to the red shift in absorption edge. The clear 1.5 and 2.7 μm Stokes emissions are presented in the Fig.5. The emission cross-section $\sigma_e$ of the $Er^{3+}$: $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transitions was calculated from absorption cross-section $\sigma_a$ via McCumber theory [7] for the cases of homogeneous and inhomogeneous broadening, see Fig.6. The case of inhomogeneous broadening leads to good match between experimentally measured and calculated emission spectra. Optical gain coefficient $G(E)$ calculated from $\sigma_e$ and $\sigma_a$ is shown in the Fig.7 as a function of relative population of the $Er^{3+}$: $^4I_{13/2}$ and $^4I_{15/2}$ manifolds [8]. $G(E)$ starts to be positive at $D \approx -0.4$ ($\approx 30$ % $^4I_{13/2}$), i.e. at relatively low pumping power. The maximal value of $G(E)$ is 2.56 cm$^{-1}$ at $\lambda \approx$ 1537 nm. These results comparing to literature [8] make the studied samples promising for EDFA and lasing. Calculated Judd-Ofelt [9,10] parameters $\Omega_2$, $\Omega_4$, $\Omega_6$ have tendency to decrease with increasing antimony content. The reason of this behavior can be seen in substitution of $[GaS_{4/2}]$ tetrahedral units with $[SbS_{3/2}]$ pyramids. This substitution results in increase of glass forming ability and thermal stability of prepared samples as evident from $\Delta T = (T_c - T_g)$ and Hruby factor $H_R$. Spectroscopic quality factor $\Omega_4/\Omega_6$ is approximately 4 higher than in commercially used YAG: $Er^{3+}$ lasers [11]. Above mentioned results give a promise for using of the studied materials for EDFA, lasing, LIDAR, etc. The compositional tuning allows to find the trade-off between thermal stability and spectroscopic properties for specific applications.

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## Conclusions

We presented the compositional tuning of the $(Ge_{25}Ga_{10-x}Sb_xS_{65})_{99.5}Er_{0.5}$ amorphous chalcogenides ($x$ = 0.5, 2.5 and 5.0 at%) allowing to find the trade-off between thermal stability and spectroscopic properties. The photon up-conversion emission was observed from green ($\lambda \approx$ 530, 550 nm) to near-infrared ($\lambda \approx$ 810, 990 nm) spectral region and it is strongly dependent on the antimony content. The substitution of $[GaS_{4/2}]$ tetrahedral units with $[SbS_{3/2}]$ pyramids results in increase of glass forming ability ($H_R$) and thermal stability ($\Delta T$) however, it causes a dramatic red shift of absorption edge which results in low up-conversion emission intensity in the green spectral region. This substitution affects local environment around $Er^{3+}$ site as is evident from Judd-Ofelt phenomenological parameters $\Omega_2$, $\Omega_4$, $\Omega_6$. The important near- ($\approx$ 1.5 μm ) and mid-infrared ($\approx$ 2.7 μm) Stokes emission bands were also observed. The spectroscopic quality factor $\Omega_4/\Omega_6$ and the results of McCumber theory ($\sigma_e$, $G(E)$, $D$) predicts these materials to be promising for EDFA and lasing at low pumping powers. The studied $Er^{3+}$-doped amorphous chalcogenides are potentially applicable for up-converters, sensors and detectors, EDFA, LIDAR and lasers. The photoluminescence intensity and quantum efficiency can be probably further increased and controlled preparing these materials in glass-ceramic state or by their shaping into photonic crystals structures.

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