Preparation and investigation of high purity Pr(3+)-doped chalcogenide glasses for active fiber optics

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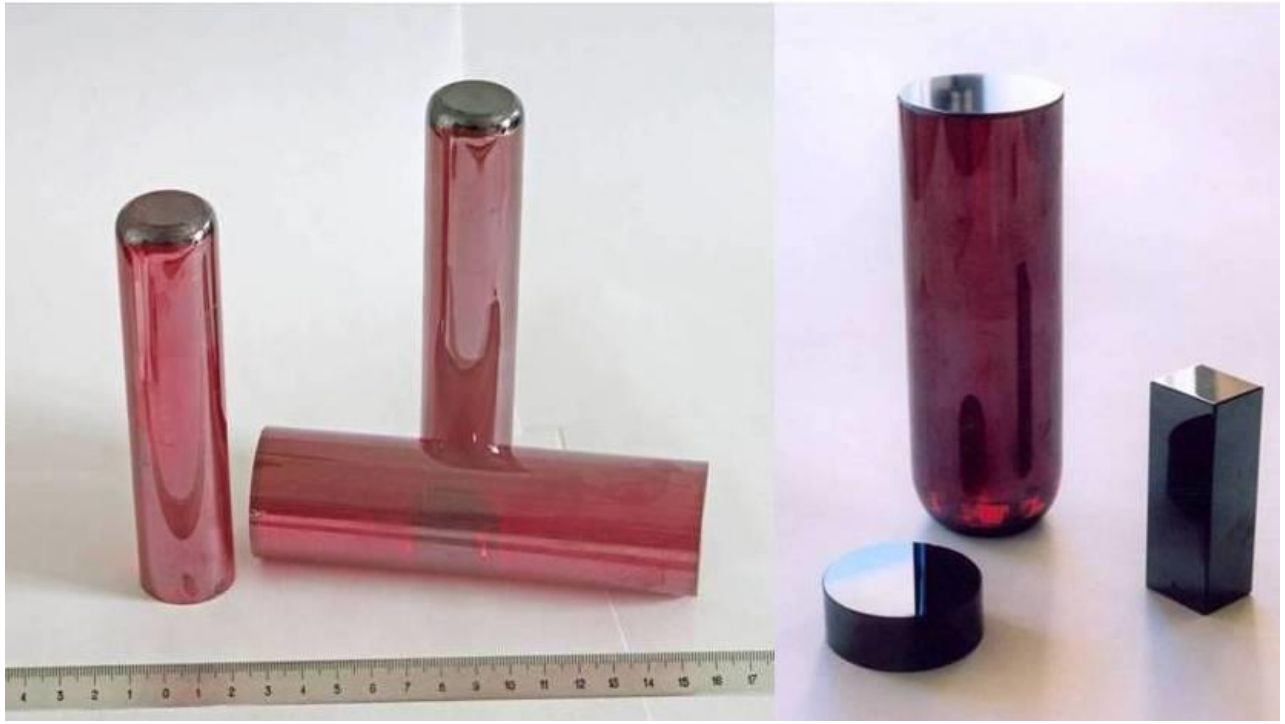
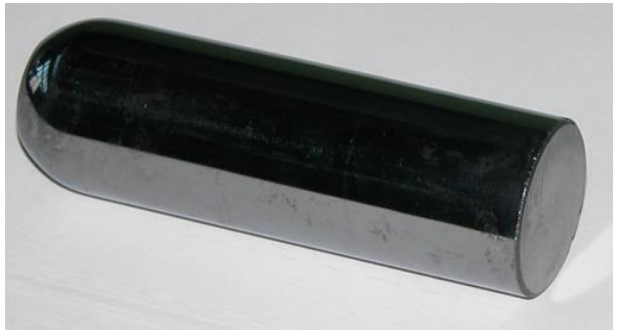
OBJECTS OF INVESTIGATIONS

Glass systems
As-S
As-Se
As-S-Se
As-Se-Te
Ge-S-(J)
Ge-Se-(J)
Ge-Sb-S-(J)
Ge-As-Se-(Ga,In,J)
Ge-Sb-Se-(Ga,In,J)
Ge-As-Se-Te
REE doped glasses

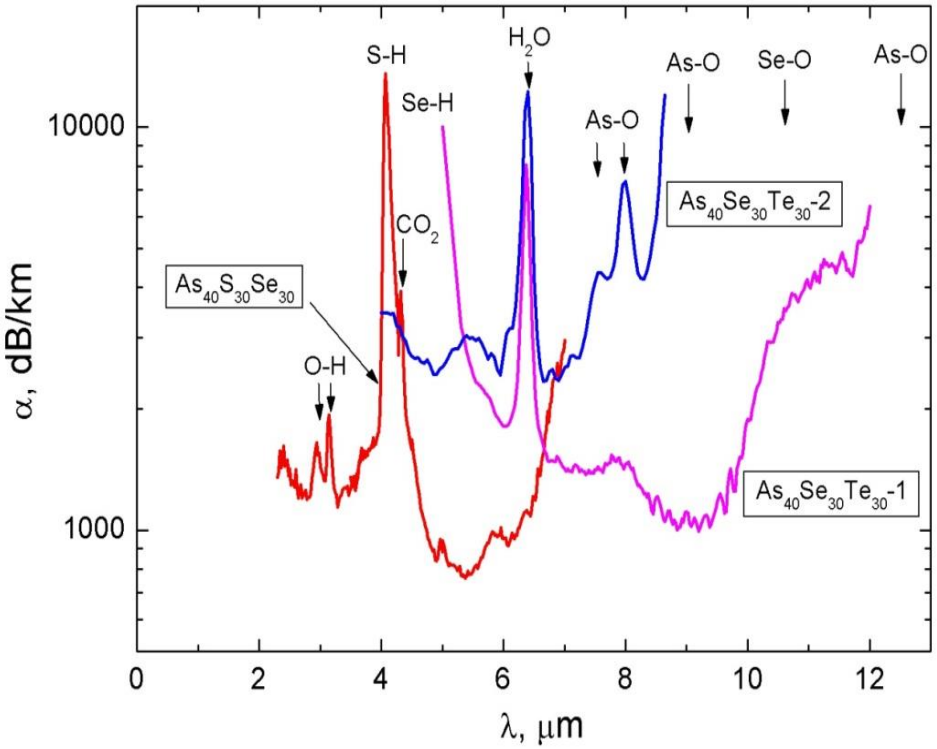




Traditional method for preparation of chalcogenide glasses:

- **Melting elements in an evacuated silica ampoule in a rocking furnace,**
- **Quenching the glass,**
- **Annealing at T_g,**
- **Slow cooling to room temperature**

Optical loss spectra of typical chalcogenide fibers from glasses prepared without purification



Main factors increased optical losses in fibers

- Absorption by limiting impurities:
  O, C, H, Si, transition metals,
- Scattering by heterogeneous inclusions,
- Tendency of glasses (melt) to micro-liquation and crystallization

<u>Requirements to impurities' content leading to intrinsic losses</u>:
Hydrogen - ≤ 0.1 ppm at;
Oxygen, Carbon, Silicon - ≤ 0.1 ppm wt;
Heterophase inclusions of submicron sizes - ≤ 10^3 cm^{-3}

Impurities content in commercial and high-purity chalcogens and arsenic

Element		Impurity content					
		H, ppm	O, ppm	C, ppm	Si, ppm	Metals, ppm	Submicron inclusions, cm^{-3} (>0.08 μm)
S	Commercial S			200-1000	>10	>10	$>10^8$
	S after purification			<0.1	0.5	<0.1	$<10^4$
Se	Commercial Se «6N»	10	8-10	43	5	>10	$5 \cdot 10^7$
	Se after double distillation	<5	<4	1	0.02	<0.5	$4 \cdot 10^5$
Te	Commercial Te «5N»		30	100-500	-	10-100	$5 \cdot 10^8$
	Te after 2x distillation		2	2-4	-	<1	$3 \cdot 10^6$
As	Commercial As «6N»		>50	10-70	2-10	1-5	$5 \cdot 10^8$
	As «6N» after 2x sublimation		≤0.1	<0.5	≤0.01	<0.05	$<1 \cdot 10^6$

The purpose

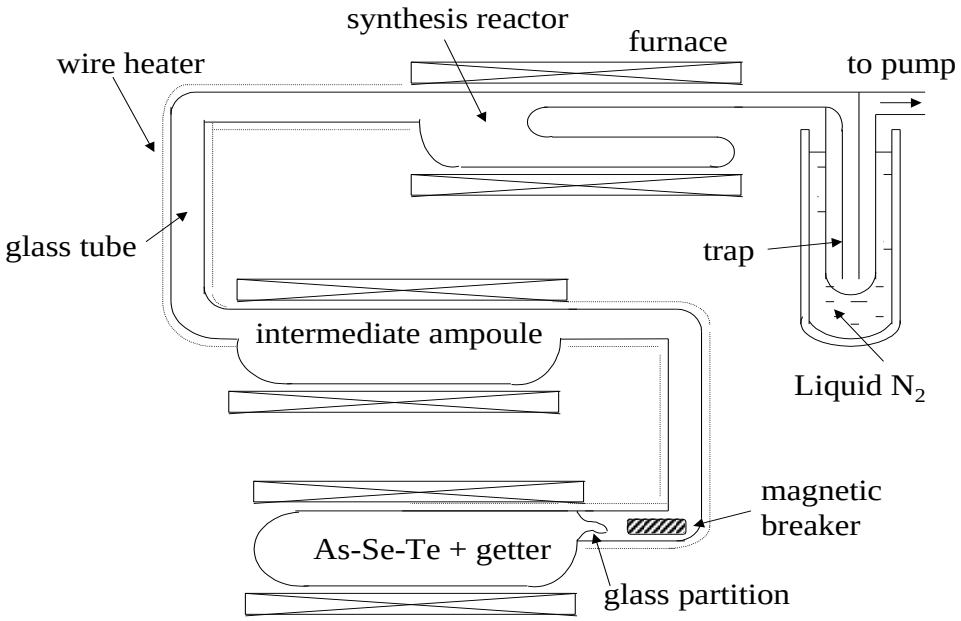
- to develop the technique for the preparation of gallium and indium-containing chalcogenide glasses with a low concentration of limiting impurities,
- to prepare Pr-doped glasses and fibers with high optical and emission properties

Stages of the preparation process of Pr-doped chalcogenide glasses are:

1) Preparation of chalcogenide glass (without gallium or indium) using the chemical-distillation method of purification.
2) Purification and an addition of the batch of metallic gallium or indium into the silica-glass reactor using a transport reaction route of metallic Ga or In transfer in a GaI_3 or InI_3 vapor flow.
3) Loading of chalcogenide glass, prepared at the stage 1, by distillation into the ampoule with metallic gallium or indium, prepared at the stage 2.
4) Homogenization of multi-component glass
5) Addition of Pr batch to prepared glass
6) Melting of Pr-doped glass with subsequent quenching, annealing and cooling

Chemical and distillation purification of glass melt using chemical getters (Al, Mg, $TeCl_4$, $AlCl_3$)

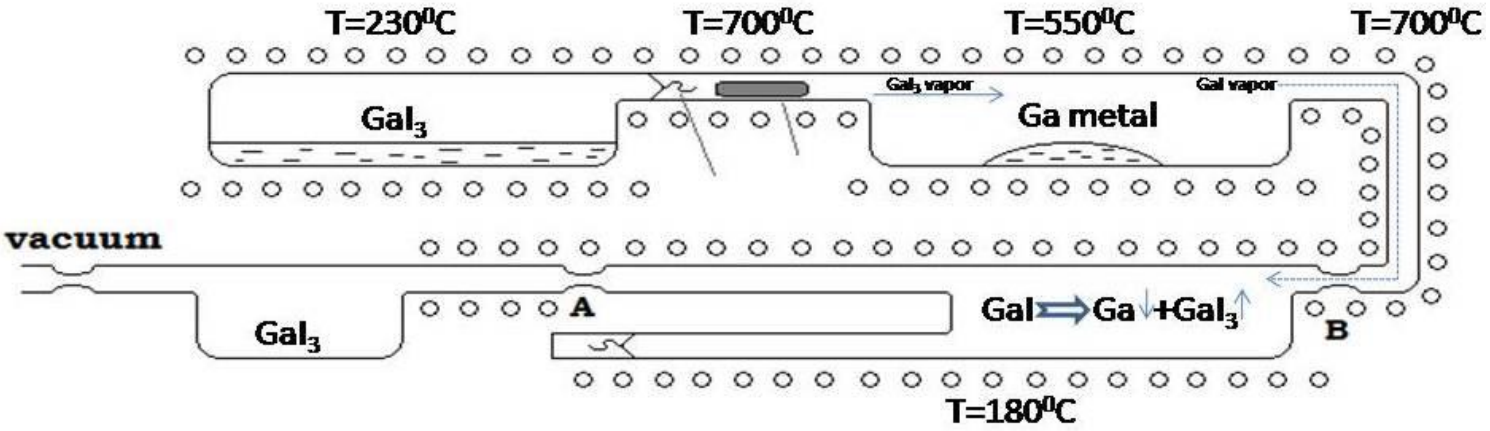
Set-up for preparation of high purity chalcogenide glasses using chemical getters

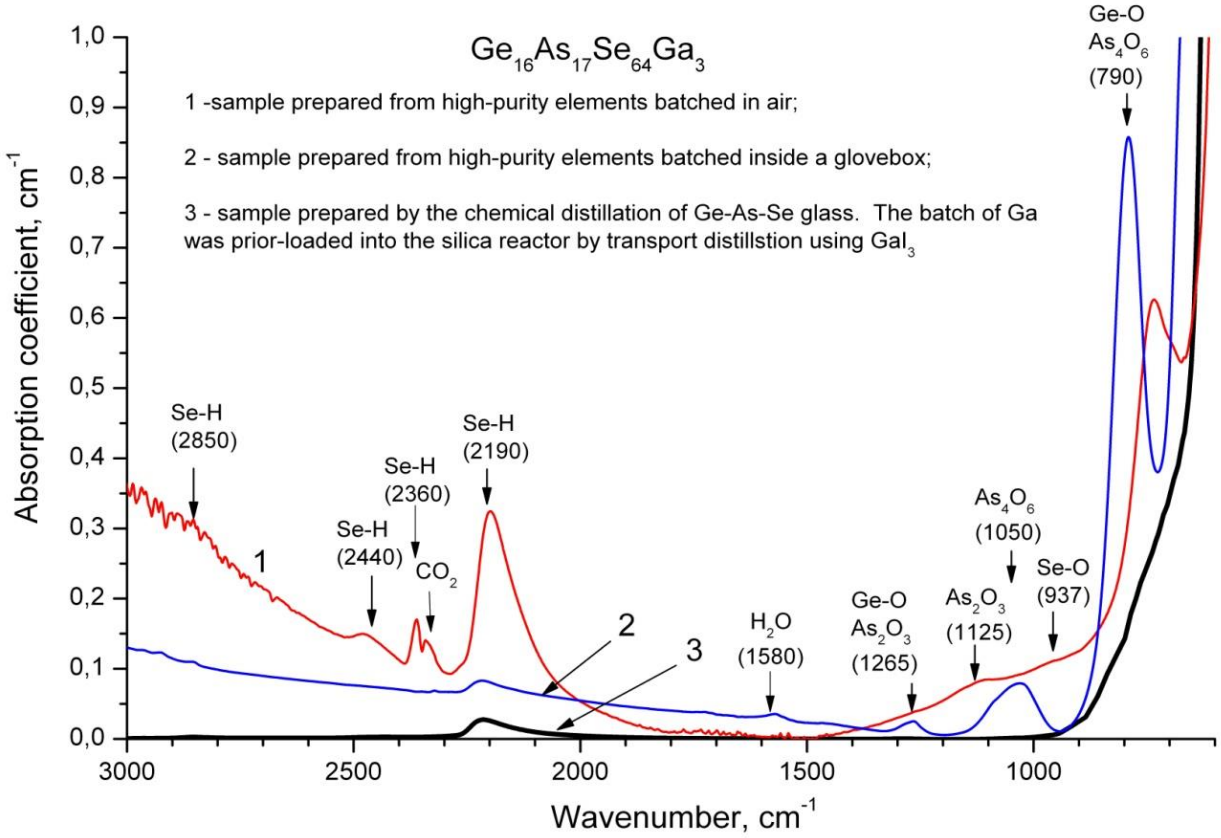


Impurity content (ppm wt.) in As-Se-Te glasses prepared by different methods

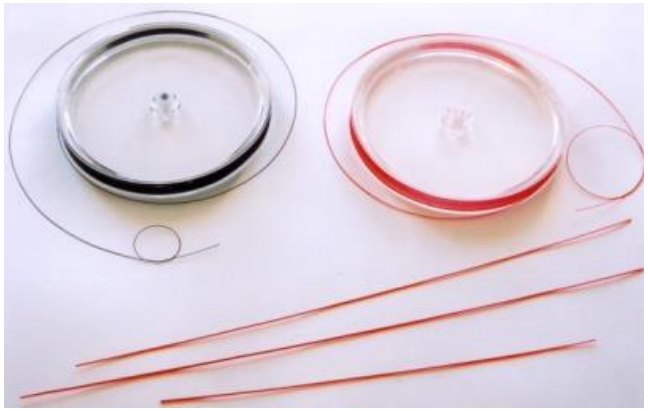
Impurity	Synthesis from elements	Melting with Al and double distillation	Melting with Al+$TeCl_4$ and triple distillation
C	1	0.6	0.2
O in the form of oxides	20	0.2	0.1
H in the form of Se-H	0.2	1	<0.01
Si	6	4	0.5
Al	<0.4	<0.5	0.1
Transition metals	0.1-1	<0.5	<0.02

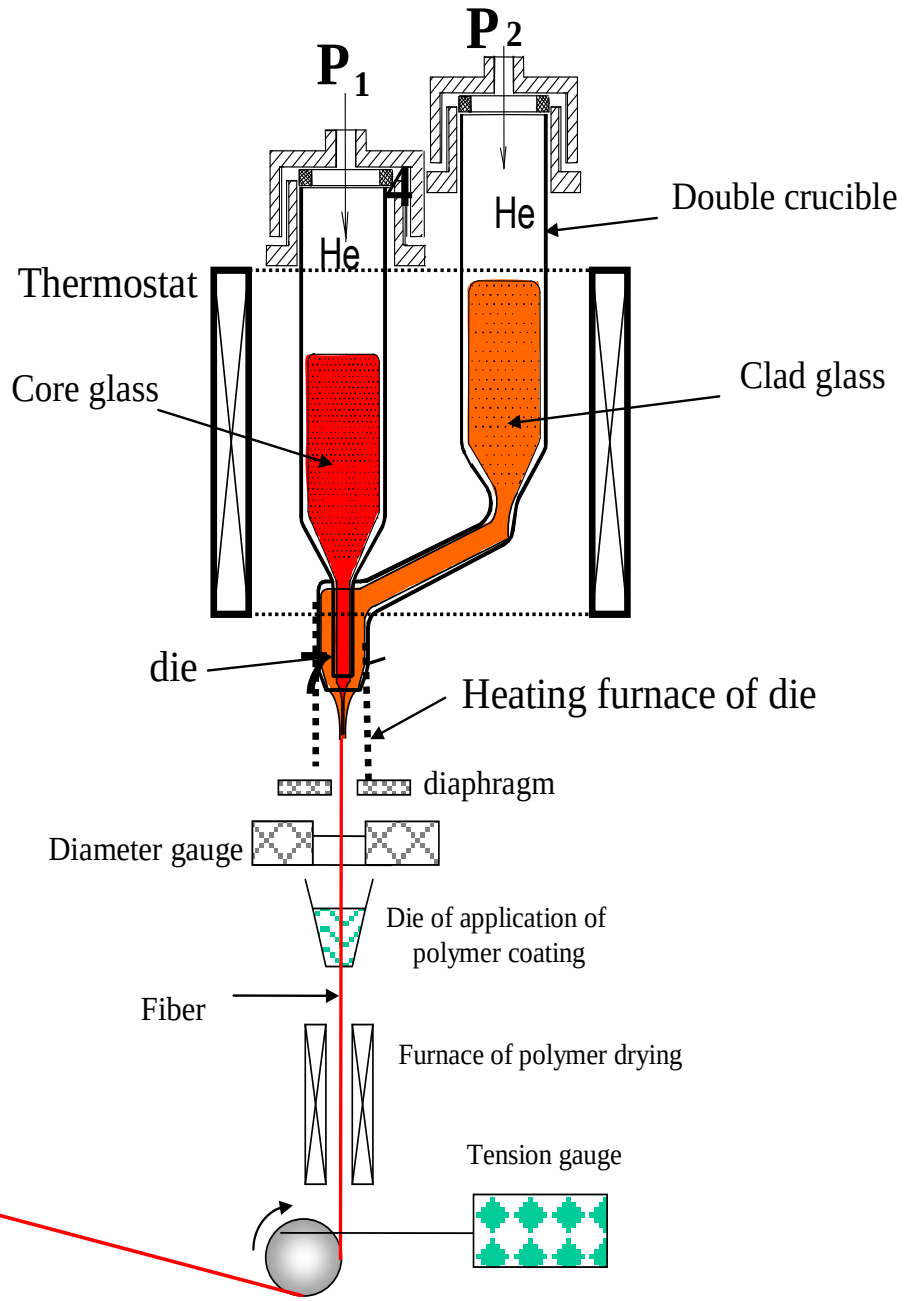
Chemical vapor transport reaction technique for preparation of high-purity Ga- or In- contained glasses





Fiber drawing





Optical losses in core-clad chalcogenide glass fibers

Glass	Type of fiber	Ordinary optical losses, dB/km	Minimum optical losses	
			β, dB/km	λ, μm
As_2S_3	Multimode	200-300	12	3.0
	Single-mode	>500	100	2.2
$As_2S_{1.5}Se_{1.5}$	Multimode	300-400	60	4.8
	Single-mode	>800	190	4.8
As_2Se_3	Multimode	300-500	≤50	6.1
As-Se-Te	Multimode	>500	<100	6.7
	Single-mode	1500-2000	330	7.5

Development of “active” glasses and fibers

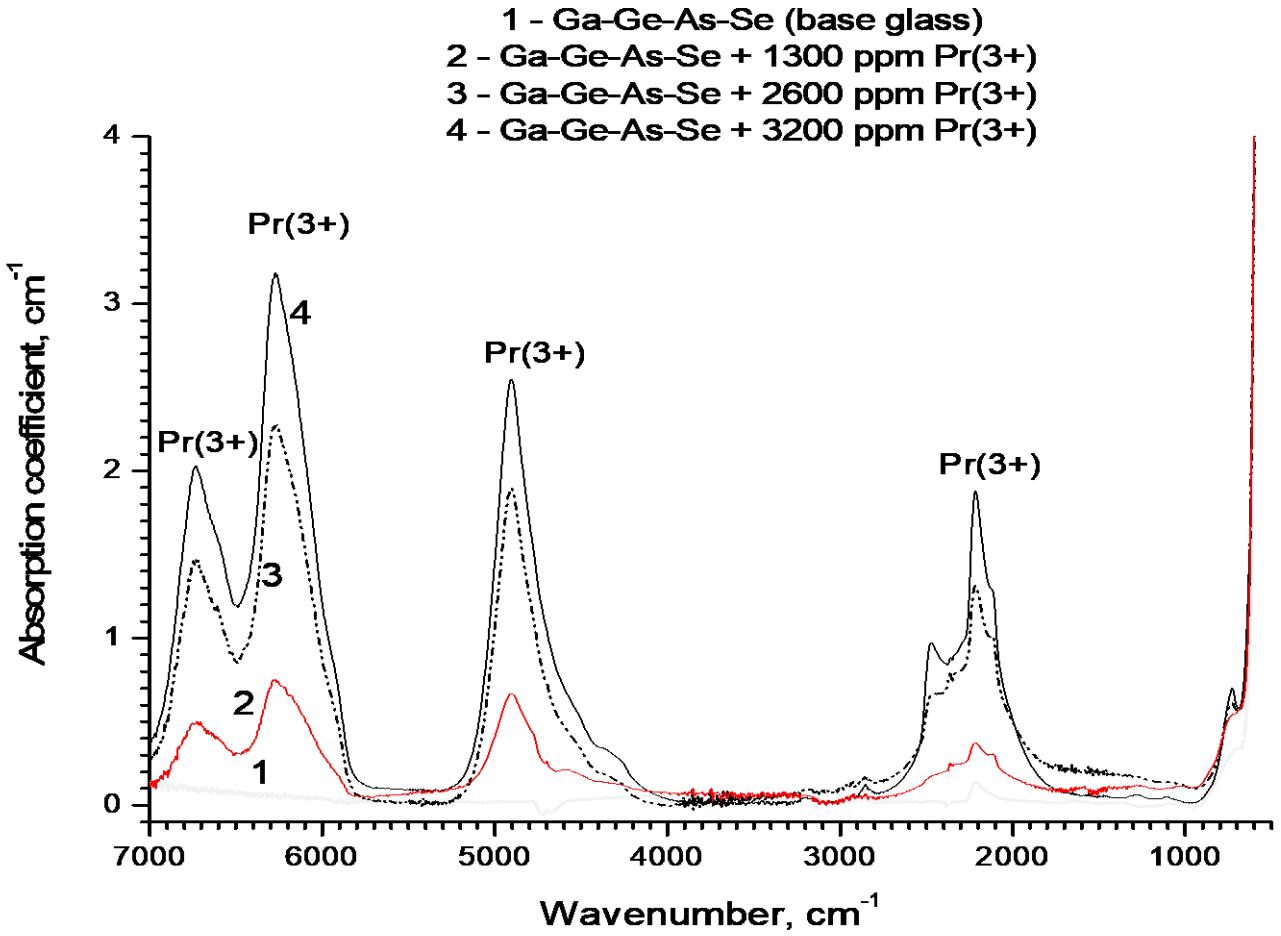
ICHPS RAS

Glass systems: Ge-As-Se-Ga(In,I) + Pr(3+)
Ge-Sb-Se-Ga(In,I) +Pr(3+)
Ge-S-I +Pr(3+)

Ga, In, J – up to 4 at.%

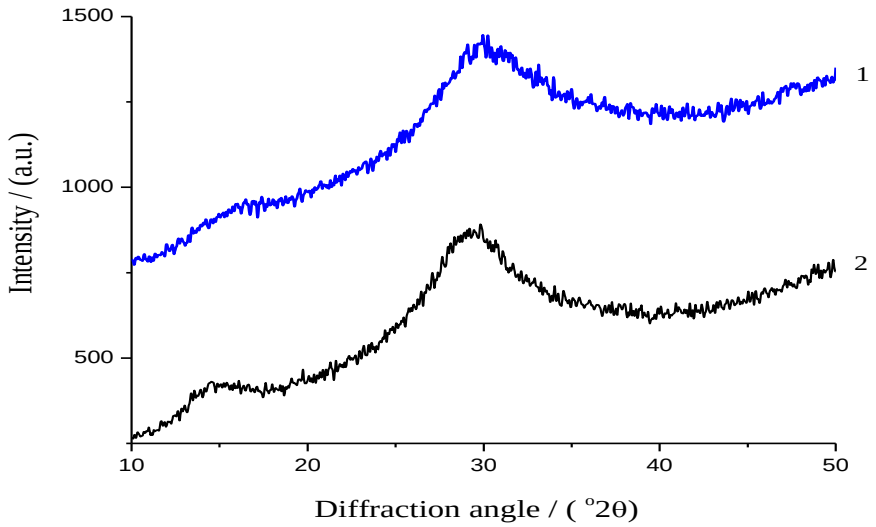
Pr(3+) in concentrations of 500÷3200 ppm – in the form of Pr_2S_3

Absorption spectra of undoped and Pr(3+)-doped Ga-Ge-As-Se glasses

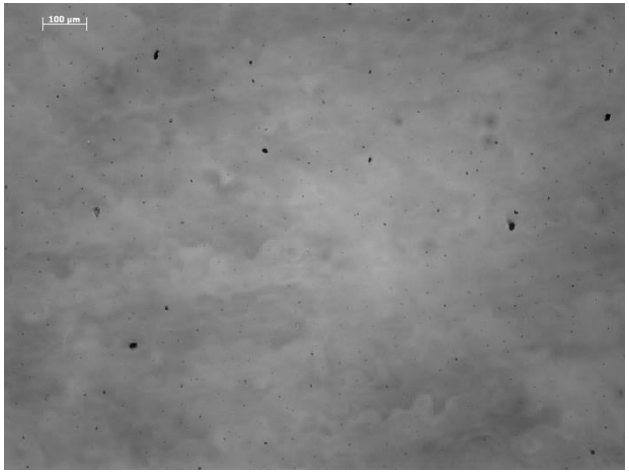


X-ray diffraction pattern of Pr-doped glasses

DSC analysis:
no crystallization

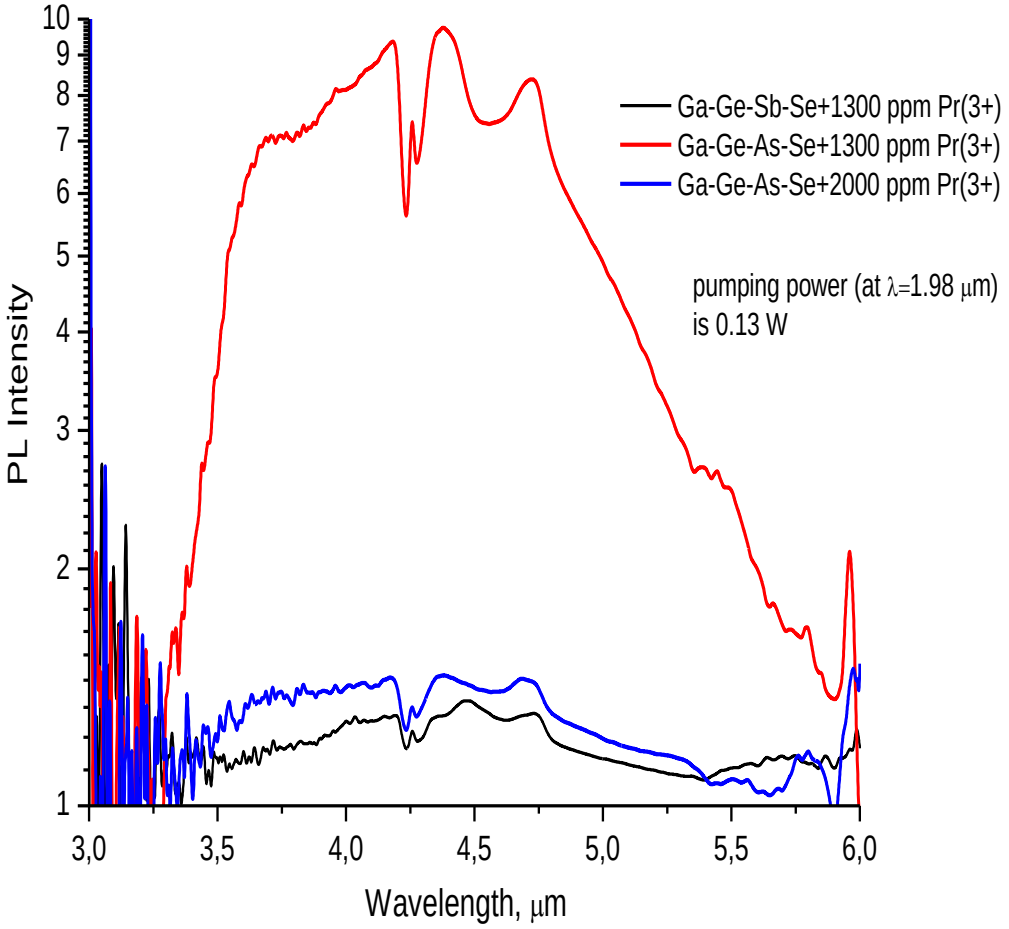


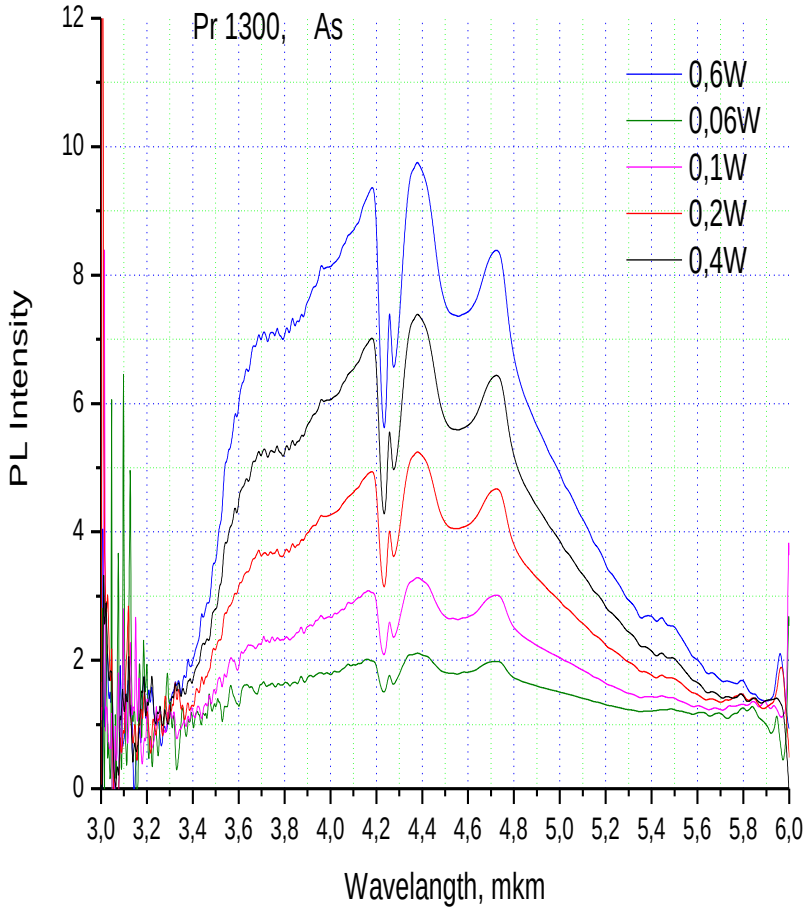
The content of submicron-sized inclusions in the host and Pr-doped glasses (methods of optical microscopy and laser ultra-microscopy)



The concentration of particles in the Pr(3+) -doped samples was from 1×10^5 to $1\times10^6 cm^{-3}$ depending on the glass composition and duration of synthesis.

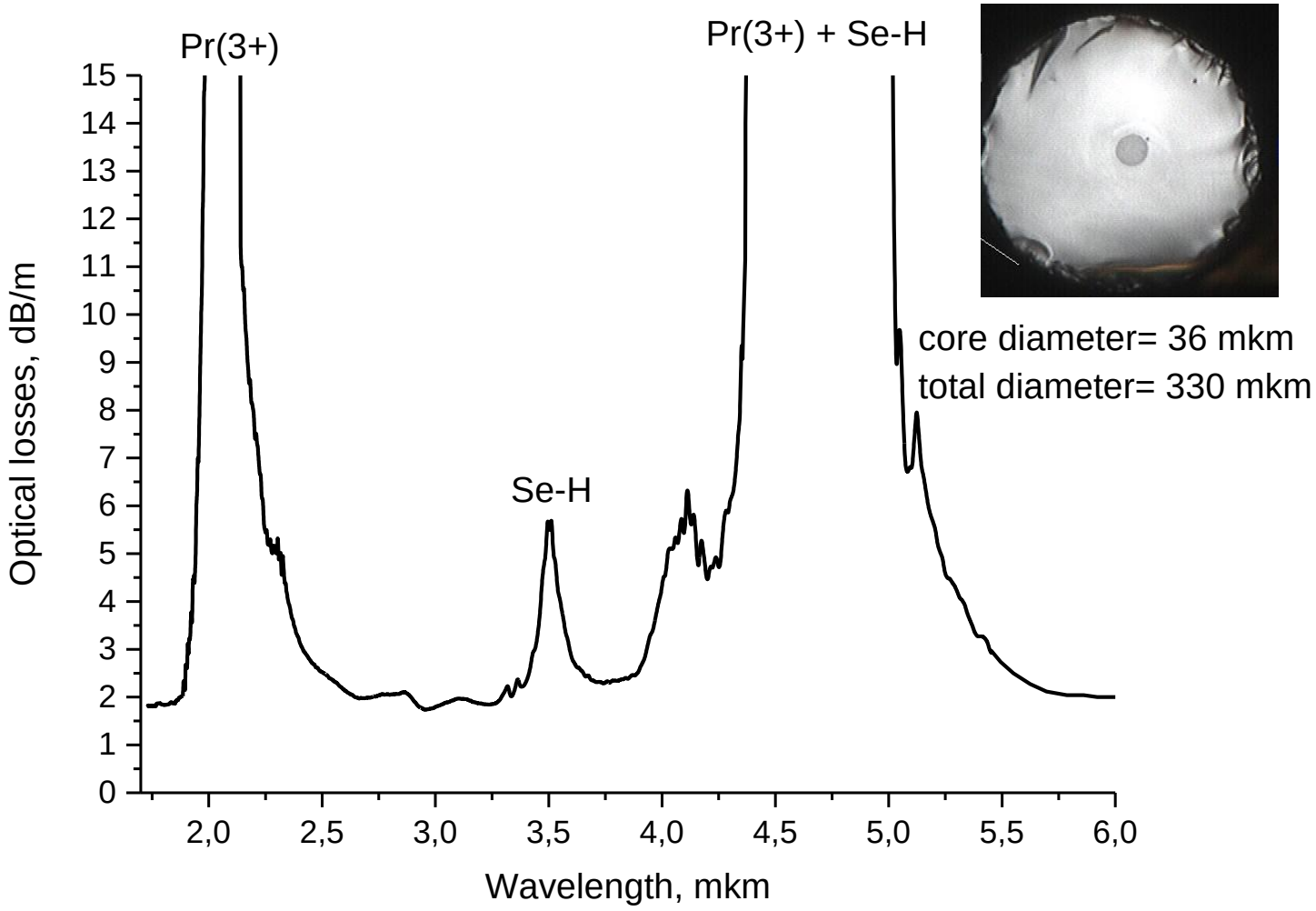
Luminescent spectra of Pr(3+) doped Ga-Ge-As-Se glasses





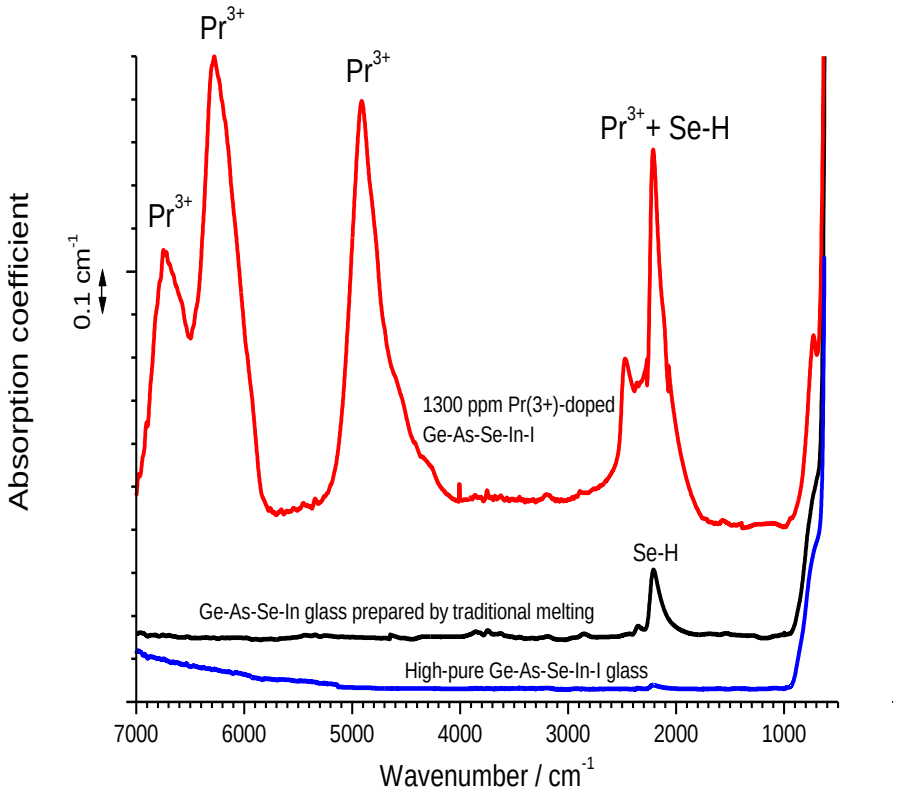
Maximum measured lifetime of emission at 4.7 μm
($^3H_4 \Rightarrow {}^3H_5$ transition) was 12 ms

Optical losses in the core-clad 1300 ppmwt Pr(3+)-doped Ga-Ge-As-Se glass fiber

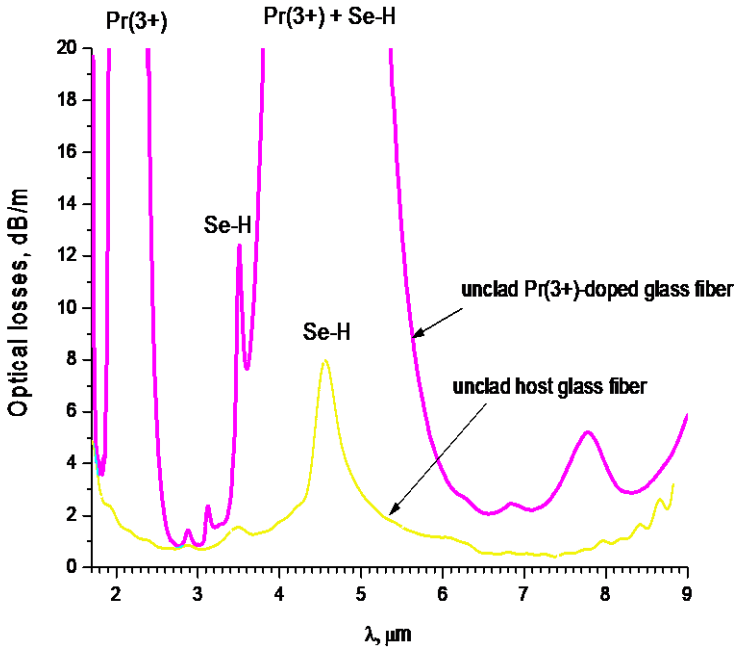


Preparation and investigation of Pr(3+)-doped Ge-As-Se-In-I glasses

Absorption spectra of bulk samples



Optical losses of single-index glass fibers



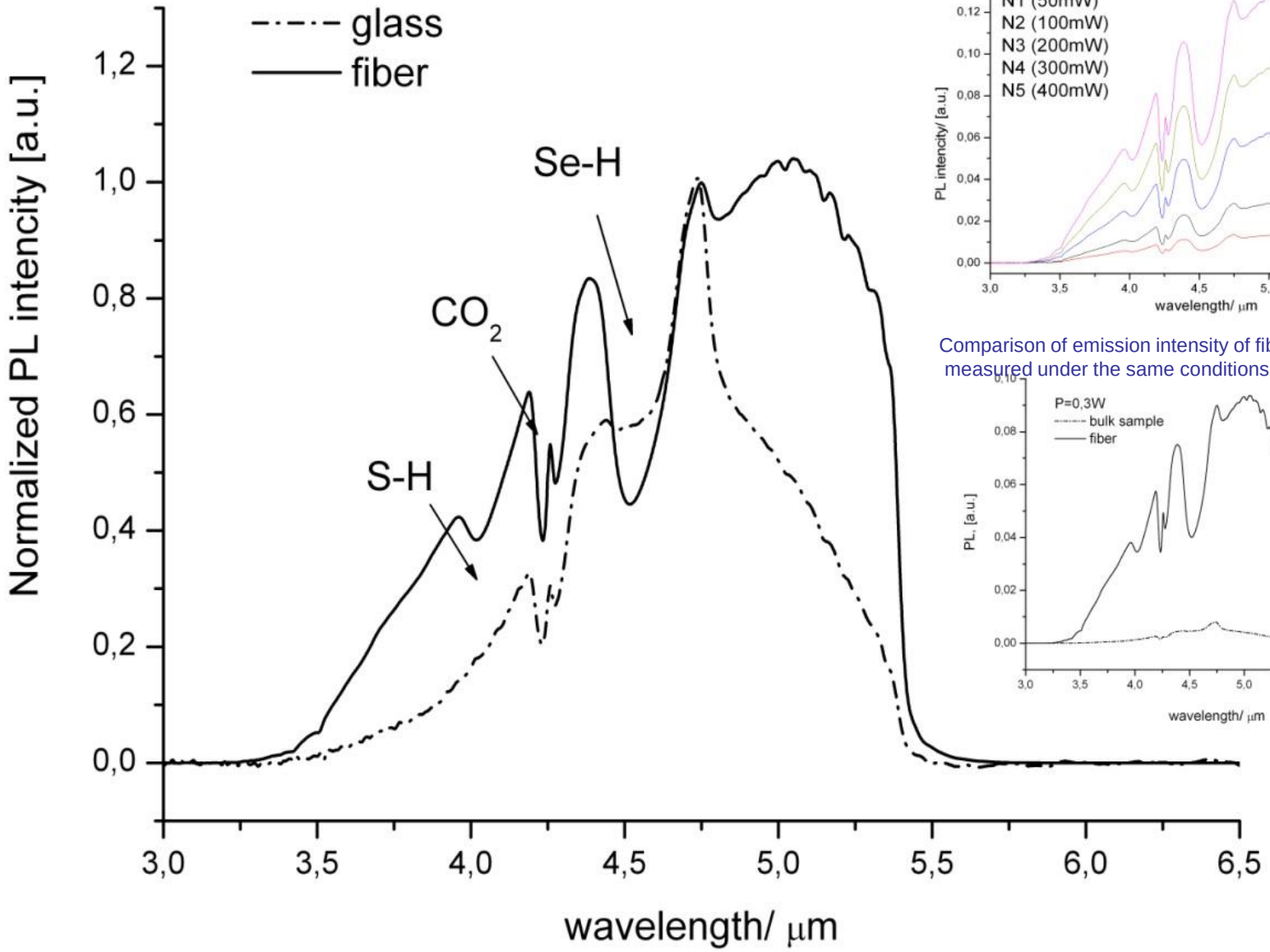
The content of impurities:

hydrogen in the form of Se-H bonds - ≤0.05 ppmwt
oxygen in the form of As-O bonds - ≤ 0.1 ppmwt

Minimum optical losses:

Host glass fiber - 0.54 dB/m at 3 μm;
0.4 dB/m at 7 μm
Pr(3+)-doped glass fiber - <1 dB/m at 3 μm

Photoluminescence spectra of 1300 ppmwt Pr^{3+}-doped Ge-As-Se-In-I bulk glass and fiber, normalized at the wavelength of 4.73 μm

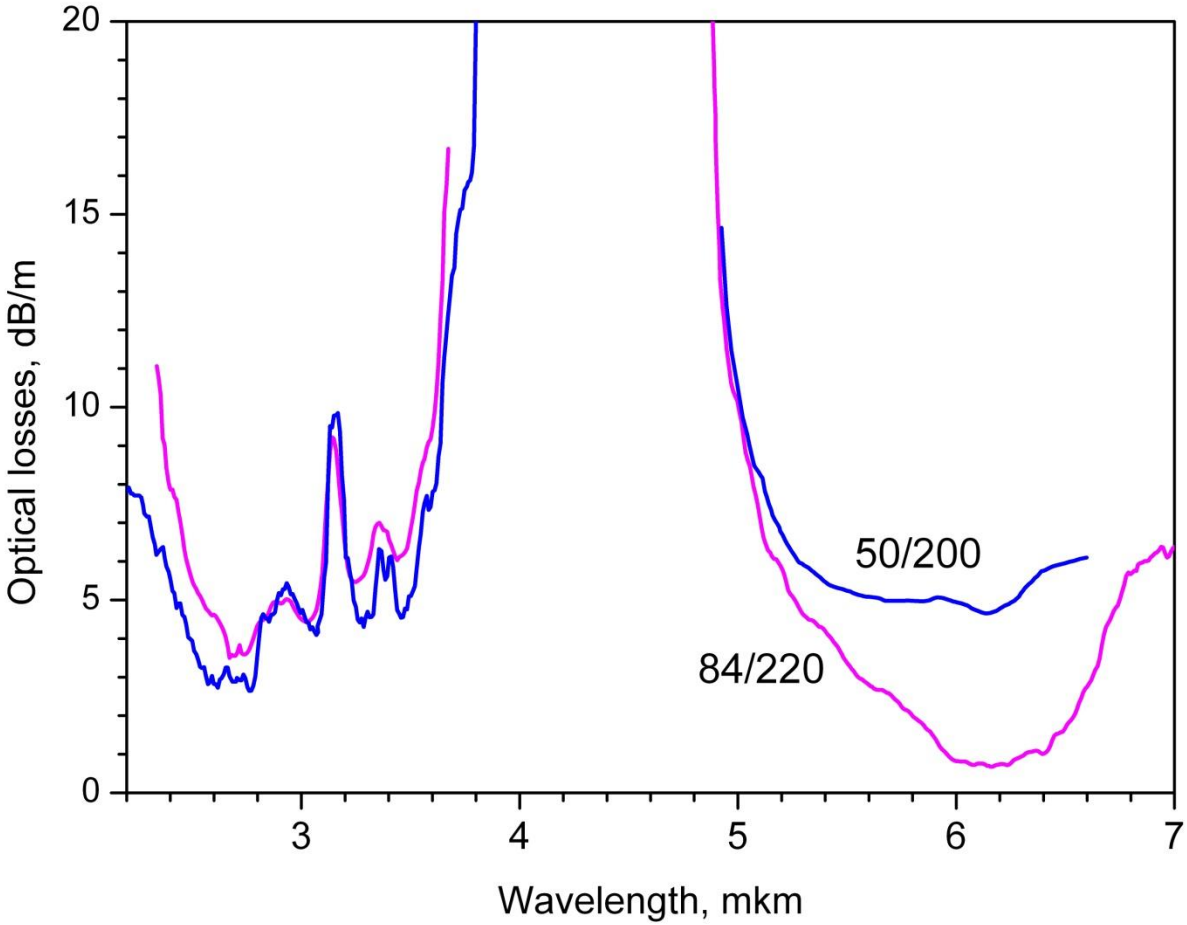


Dependence of measured emission intensity of the fiber on the pump power intensity

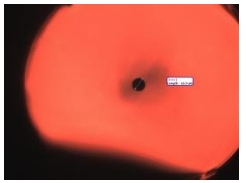
Comparison of emission intensity of fiber and bulk sample measured under the same conditions of pumping.

Optical losses of core-clad fibers

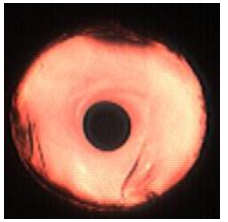
core – Ge-As-Se-In-I+2000ppm Pr(3+)
clad – Ge-As-S



Core dia / clad dia
= 16/200 μm



Core dia / clad dia
= 50/200 μm



Core dia / clad dia
= 84/220 μm

Summary

- **The multi-stage method for preparation of Pr(3+) doped chalcogenide glasses with low content of limiting impurities have been developed.**

- **The prepared Pr(3+)-ions-doped chalcogenide glasses have a high optical transparency in the mid-IR, a low concentration of scattering particles, and a low tendency to crystallization.**

- **The content of impurities in the purest glass samples was by 10–50 times lower than that in glasses manufactured by the traditional direct method.**

- **The prepared doped glasses and fibers exhibit an intensive photoluminescence in the spectral ranges of 1.3-2.5 and 3.5-5.5 μm.**