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Journal of Alloys and Compounds 300–301 (2000) 398–406

Journal of
ALLOYS
AND COMPOUNDS

www.elsevier.com/locate/jallcom

Er³⁺ and Yb³⁺ doped active media for ‘eye safe’ laser systems

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Abstract

There is considerable interest in compact pulsed high peak power laser sources emitting at wavelengths near 1.55 μm. Rangefinders and other applications with free space propagation could be a benefit of such devices. The wavelength of around 1.55 μm is in the eyesafe regime where significantly higher pulse energies can be used without damaging human eyes. Erbium- and ytterbium-doped YAG single crystals were obtained by the Czochralski method. The basis conditions of growth and the results of optical homogeneity measurements of the obtained crystals are presented. This report describes also the effect of variations of erbium, ytterbium, chromium ions and glass base compositions on laser efficiency and the improved properties of a new glass base. The spectral properties and laser characteristics were investigated. Absorption spectra of Er³⁺- and Yb³⁺-doped active media were measured in the spectral range 190 to 5000 nm at room temperature. Excitation and luminescence spectra were also recorded at room temperature with a Jobin-Yvon spectrofluorometer using a diode laser (Polaroid 4300, 980 nm, 1 W) as an excitation source. The measurements of the lifetime of the Er³⁺ ions in the upper laser level (⁴I_{13/2}) of the samples were made by the direct method with pulse excitation. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Human eye damage; Safety; Laser systems

1. Introduction

The spectral range of ‘eye safe’ laser radiation wavelength results from the optical characteristics of the eye [1]. Radiation shorter than 400 nm and longer than 1400 nm is strongly absorbed by tissues so it does not penetrate the eye inside and does not cause retina damage. A wavelength of 1.5 μm is considered as a safe one for direct looking at the radiation beam of energy density a hundred times higher than for 10.6 μm (CO₂ laser) and 2×10⁵ times higher than for wavelength of 1.06 μm (Nd:YAG laser) [2].

In the first laser systems generating eyesafe radiation, a Raman shifter was used in the form of a methane cell in which a conversion of radiation, generated by YAG:Nd³⁺ (λ=1064 nm), into radiation of wavelength of 1.54 μm occurred. Molecular crystals (e.g. Ba(NO₃)₂, CaCO₃, or CaSO₄), in which the effect of forced Raman scattering occurs, are competitive with high-pressure gaseous cells. Because the efficiency of this process is not high, these systems have not found practical applications [3].

Parametric generation of wavelengths near 1.5 μm in nonlinear crystals was practically not used. The main obstacle in this case is the difficulty to ensure stable laser operation within a wide range of temperatures [4].

At the beginning of the 1990s an erbium–ytterbium–phosphate glass was used for the first time for generation of laser radiation at the wavelength of 1.5 μm [5]. The laser systems including this active material have found many practical applications [6,7].

The drawback of phosphate glass is its low thermal and mechanical stability. So, new research is carried out for higher resistant glass matrices and crystalline media [8].

In the crystals used for the systems generating eyesafe radiation, the most frequently active dopants are Er³⁺ and Cr⁴⁺ ions [9]. Yb³⁺ ions are used in crystalline media doped with Er³⁺ in order to increase the excitation efficiency, especially in the laser diode pumped systems.

The aim of the work was to determine the growth conditions of yttrium–aluminium–garnet crystals doped with Er³⁺ and Yb³⁺ ions (YAG:Er³⁺, YAG:Nd³⁺, Yb³⁺) of various concentration and to examine these crystals in respect to their application as active media for lasers generating eyesafe radiation.

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Erbium-doped optical glasses are effective media for active lasers generating eyesafe radiation of a wavelength $1.54 \mu\text{m}$ [10–15]. Development of erbium glass laser systems requires investigations aimed at improvement in glass properties and increase in effectiveness of laser generation. Operation of flashlamp-pumped erbium glass lasers is limited by low repetition rates. It is caused by low heat conduction and weak thermal-proofing of the glasses [16,17]. The purpose of the investigations described here was the determination of the influence of the doping level as well as of the changes in the constitution of the glass matrix on the resistance of the glass rods against thermal shock and the laser yield [18]. The presence of hydroxyl groups (OH^-) is an important factor influencing the glass structure. In glasses having a high concentration of hydroxyl ions, strong quenching of the fluorescence occurs and a reduction of the lifetime of excited Er^{3+} ions was observed [18]. In such a case an absorption band near $2.2 \mu\text{m}$ is observed. The number of OH^- groups can be reduced by adequate melting of glass and its annealing.

2. Crystal growth

The crystals were obtained by the Czochralski method, using iridium crucibles of external dimensions $\phi 50 \times 50 \times 1.5 \text{ mm}$. The insulating housing of the crucible was made of alundum ceramics and granular zirconium ceramics stabilised with hafnium ($\text{ZrO}_2\text{:HfO}_2$) that filled the space between the crucible, the tube, and alundum base.

The crystallisation processes were carried out in nitrogen atmosphere containing a small amount (a fraction of a percentage) of oxygen. High purity oxides $\text{Y}_2\text{O}_3(5\text{N})$ and $\text{Al}_2\text{O}_3(5\text{N})$ from J.M. & PROD., Er_2O_3 and $\text{Yb}_2\text{O}_3(5\text{N})$ from Aldrich were used as initial materials.

Crystals of a diameter of about 25 mm and a length of 60 mm with the following compositions were obtained:

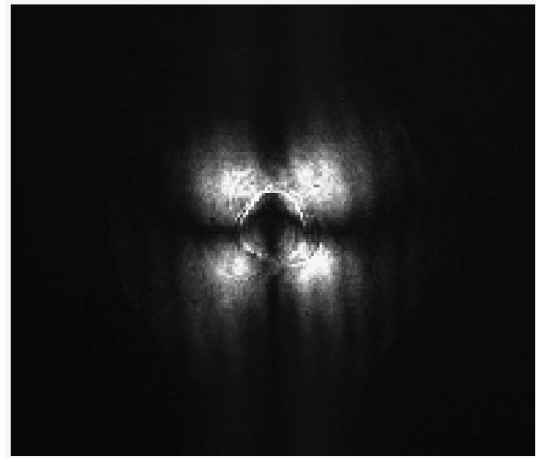


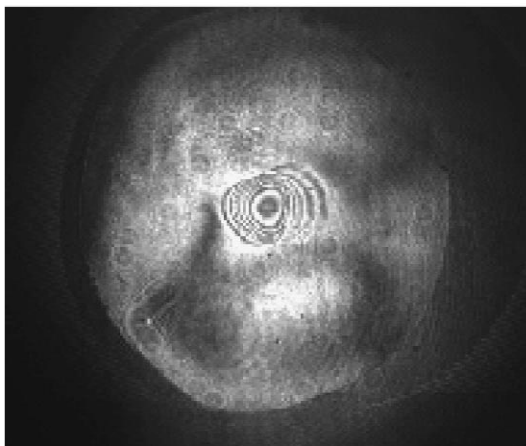
Fig. 2. Elastoscopic picture obtained for the YAG:Er^{3+} crystal no. 1 of length 60 mm.

YAG:Er^{3+} (1.5% Er^{3+})
 $\text{YAG:Er}^{3+}, \text{Yb}^{3+}$ (0.9% Er^{3+} , 9% Yb^{3+})
 $\text{YAG:Er}^{3+}, \text{Yb}^{3+}$ (0.5% Er^{3+} , 5% Yb^{3+}).

In all crystals obtained the core area of the characteristic threefold symmetry was found. The core has clear, sharp boundaries and its area has a diameter of about 2 mm. On the basis of the investigations carried out with a Mach-Zender interferometer it was stated that the crystals in the core area are characterised by an inhomogeneity of the refractive index due to defects and stresses. Out of the core area all of the crystals were optically homogeneous. Characteristic interferograms obtained for a YAG:Er^{3+} crystal are shown in Fig. 1.

The stress in the crystals was examined using the elastoscopic method and registering the picture obtained for crystal, placed between crossed polarisers. Fig. 2 shows the results of examinations performed for the YAG:Er^{3+} crystal.

a)



b)

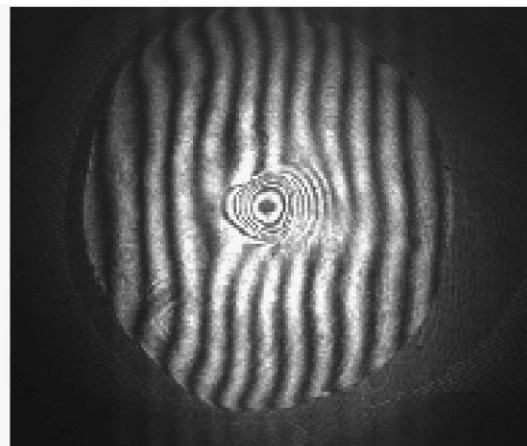


Fig. 1. Interferograms obtained for the YAG:Er^{3+} crystal no. 1 of length 60 mm; (a) zero-fringe order, (b) multi-fringe field.

On the basis of the interferometric and elastoscopic investigations the areas of the crystal cuts were determined in order to perform optical elements for the investigation of the spectroscopic characteristics.

3. Synthesis of glasses

Based on literature data three matrix glasses were chosen for investigation

- PEY-00 belonging to the oxide system $P_2O_5-Al_2O_3-BaO-K_2O$,
- PEY-10 of the constitution modified in comparison with PEY-00 glass, due to reduction of Al_2O_3 amount and increase in B_2O_3 in order to decrease melting and fining temperatures. So, PEY-10 is a glass from the $P_2O_5-Al_2O_3-B_2O_3-BaO-K_2O$ oxide system,
- PEYPb-00 belonging to the oxide system $P_2O_5-B_2O_3-Al_2O_3-PbO-BaO-Na_2O$.

The following doping level of the manufactured glasses was chosen:

- 12% mas. Yb_2O_3
- 0.3% mas. Er_2O_3
- 0.04% mas. Cr_2O_3 .

In each of the three groups of examined glasses, the first glass is a matrix one (with no dopants), the second glass is

Yb_2O_3 and Er_2O_3 doped glass, the third glass is a glass with three kinds of dopants, i.e. Yb_2O_3 , Er_2O_3 , and Cr_2O_3 .

For glass melting the raw materials 'pure for analysis' were used. Synthesis was carried out in a silica crucible.

The glasses of the PEY-00 series (PEY-00, PEY-01, PEY-02) were melted at the highest temperatures (maximal melting and clarifying temperatures of 1370°C). The glasses of the PEY-10 series (PEY-10, PEY-11, PEY-12) can be melted at lower temperatures (max. temperature 1350°C). The easiest for melting are lead-phosphate glasses of PEYPb-00 series (PEYPb-00, PEYPb-01, and PEYPb-02) (max. temperature 1300°C).

The glass samples obtained were well melted (with no solid inclusions), clear (with no gaseous inclusions), and homogeneous. There were no observed spontaneous glass crystallisation during its self-cooling in a mould. After being removed from the furnace, stress relief was observed using an optical microscope. Neither superficial crystallisation nor bulk crystallisation were found.

4. Investigations of glass properties

The fundamental physical properties of the melted glasses are listed in Table 1. The measurements of refractive index were made using an Abbe refractometer.

Characteristic temperatures in the reologic curve are determined by dilatometric examinations (quartz differential dilatometer of the Baehr firm 801 type) and examinations performed with a Leitz thermal microscope. Glass density was determined by means of hydrostatic weighing

Table 1
Fundamental physical properties of the investigated phosphate glasses doped with Yb_2O_3 , Er_2O_3 , and Cr_2O_3

Type of glass	PEY-						PEYPb-		
	00 ^a	01	02	10 ^c	11	12	00 ^a	01	02
Refractive index n_d	1.5282	1.5322	1.5325	1.5282	1.5325	1.5323	1.5765	1.5778	1.579
Coefficient of linear expansion for the range of 20 to 300°C α [$10^{-7} K^{-1}$]	84.3	80.4	78.6	84.2	78.7	79.3	104.6	84.6	86.1
Lower annealing temperature t_{low} [°C] $\log \eta=14.6$	552	552	554	530	553	553	424	477	470
Transformation temperature T_g [°C] $\log \eta=13.4$	588	581	589	565	585	588	470	500	499
Upper annealing temperature t_{up} [°C] $\log \eta=13.0$	595	589	596	573	595	600	484	507	506
Dilatometric softening temperature DST [°C] ($\log \eta=11.0$)	632	632	635	621	632	637	524	546	544
Characteristic temperatures in the Leitz thermal microscope [°C]									
Temperature of:									
sample rounding T_r ($\log \eta=9.0$)	660	660	660	650	670	640	555	580	580
sphere formation T_s ($\log \eta=6.0$)	770	770	785	780	790	795	660	710	710
hemisphere formation T_h ($\log \eta=4.0$)	880	870	900	880	885	840	700	745	765
sample spreading T_{sp} ($\log \eta=2.0$)	930	1000	960	940	950	980	1100	820	870
Density ρ [g/cm^3]	2.69	2.85	2.83	2.66	2.84	2.88	3.04	3.20	3.26
Crystallisation according to observation in the Leitz thermal microscope	a	b	a	a	a	a	c	a	d
Crystallisation according to DTA data	No crystallisation								

^a No crystallisation.

^b Few crystalline forms.

^c Weak crystallization.

^d Very weak crystallisation.

^e These columns correspond to matrix glasses (with no active dopants).

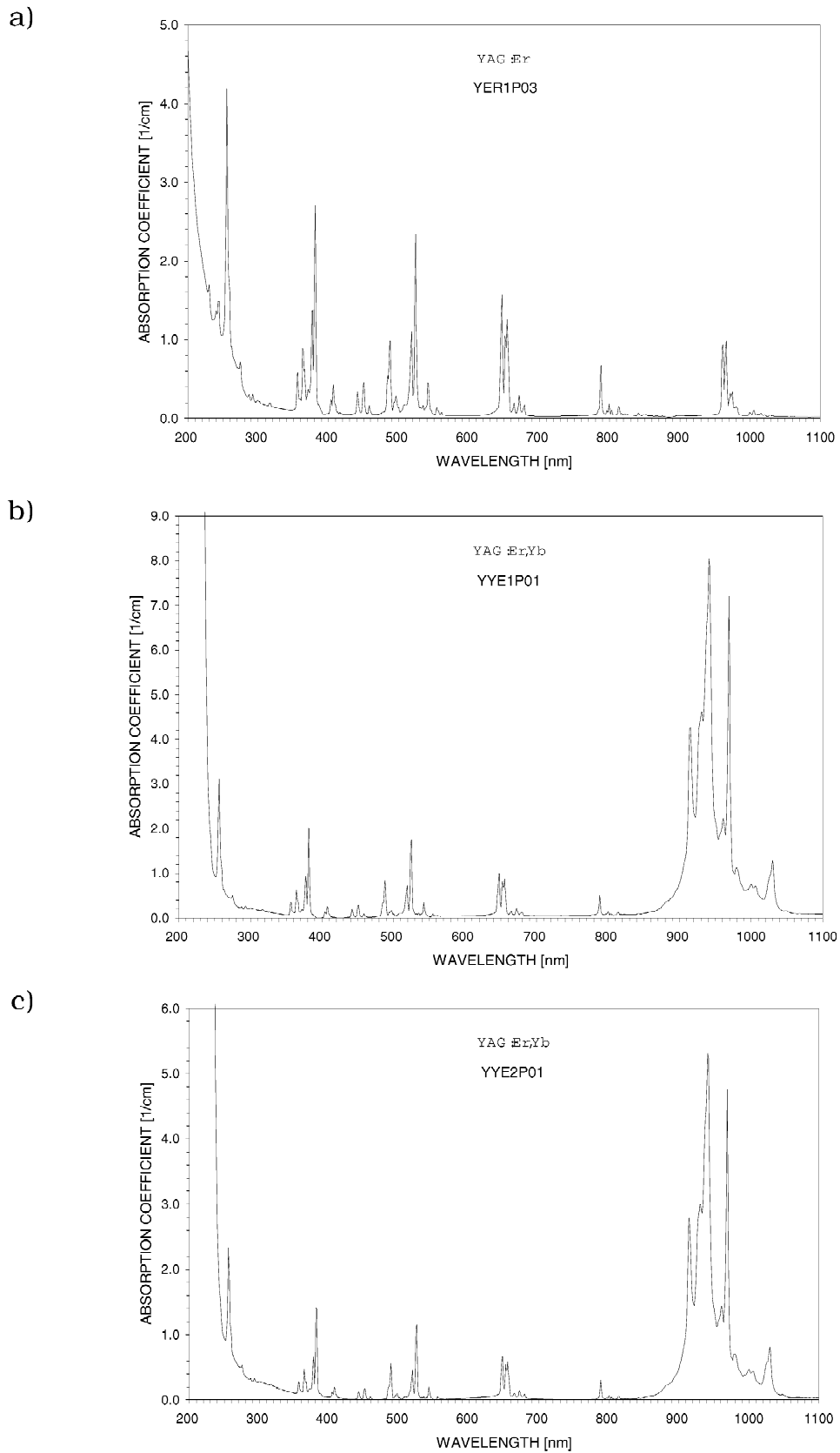


Fig. 3. Spectra of the absorption coefficient of erbium- and ytterbium-doped YAG crystals (a) YAG:Er³⁺ (1.5 at.% Er³⁺), (b) YAG:Er³⁺, Yb³⁺ (0.9 at.% Er³⁺, 9 at.% Yb³⁺), (c) YAG:Er³⁺, Yb³⁺ (0.5 at.% Er³⁺, 5 at.% Yb³⁺).

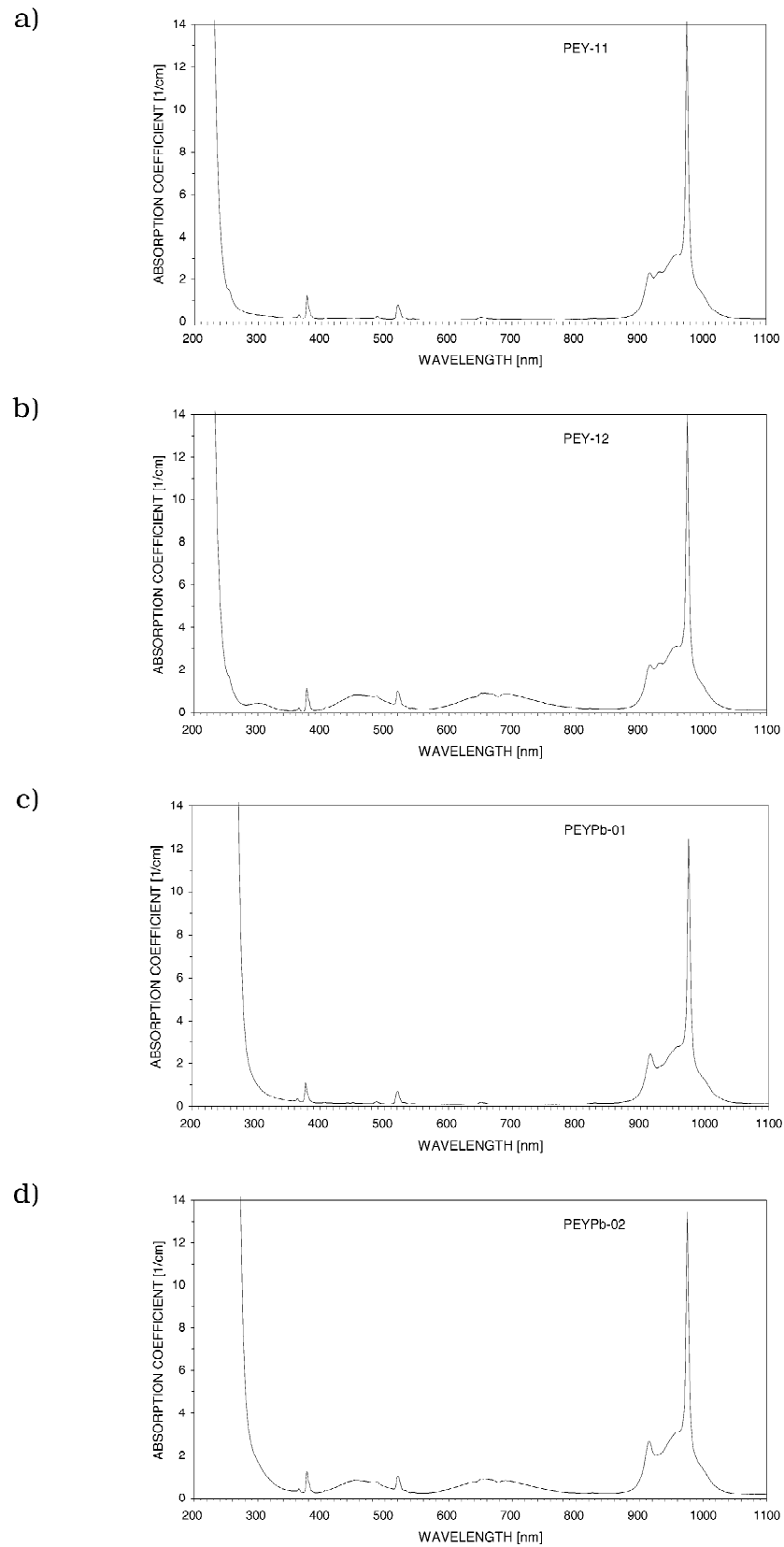


Fig. 4. Spectra of the absorption coefficient of PEY-11 (a), PEY-12 (b), PEYPb-01 (c), and PEYPb-02 (d) glasses.

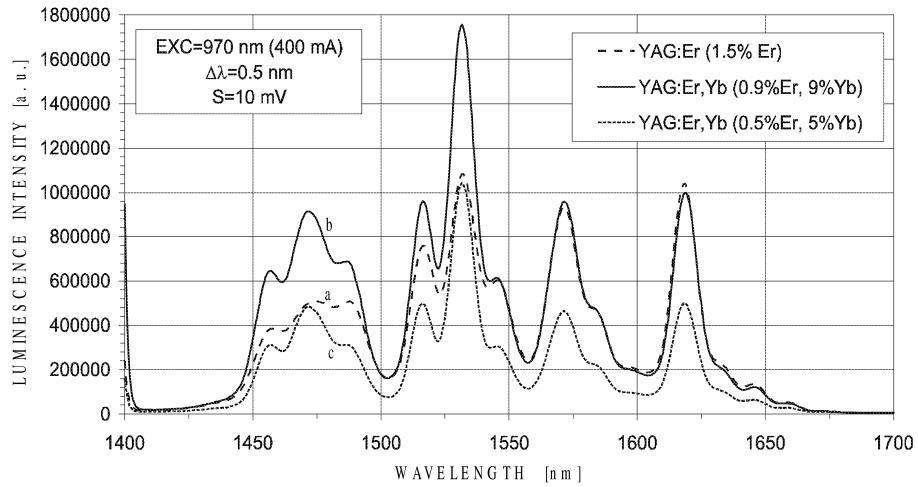


Fig. 5. Luminescence spectra of the erbium- and ytterbium-doped YAG crystals (a) YAG:Er³⁺ (1.5% Er³⁺), (b) YAG:Er³⁺, Yb³⁺ (0.9% Er³⁺, 9% Yb³⁺), (c) YAG:Er³⁺, Yb³⁺ (0.5% Er³⁺, 5% Yb³⁺).

method. Crystallisation was observed in a thermal microscope and determined on the basis of differential thermal analysis (DTA).

5. Spectroscopic investigations

From the crystals and glasses obtained, plane-parallel plates of a thickness of 1 mm were cut, ground, and polished for spectral measurements. In order to determine the dependence of the absorption coefficient on wavelength $k(\lambda)$, the transmission was measured as a function of the wavelength. The measurements were carried out within the spectral range of 200 to 1100 nm ($\Delta\lambda=1$ nm) using a LAMBDA2 Perkin Elmer spectrophotometer, within the range of 1100 to 1500 nm ($\Delta\lambda=1$ nm) using an ACTA MVII Beckman spectrophotometer, and within the range of

1.5 to 25 μm ($\Delta 1/\lambda=1$ cm⁻¹) using a Fourier Perkin Elmer spectrophotometer 1725-X FT-IR.

The absorption coefficient was calculated with consideration of multiple reflections of the radiation inside the sample:

$$k(\lambda) = \frac{1}{d} \ln \frac{1}{T_r(\lambda)}$$

where

$$T_r(\lambda) = \frac{\sqrt{(1 - r_f)^4 + 4 \cdot r_f^2 \cdot T(\lambda)^2} - (1 - r_f)^2}{2 \cdot T(\lambda) \cdot r_f^2}$$

$T(\lambda)$ is the measured value of the sample transmission, d is the sample thickness, r_f is the Fresnel reflection coefficient.

The spectra of the absorption coefficient for Er³⁺- and Yb³⁺-doped YAG crystals are shown in Fig. 3. Fig. 4

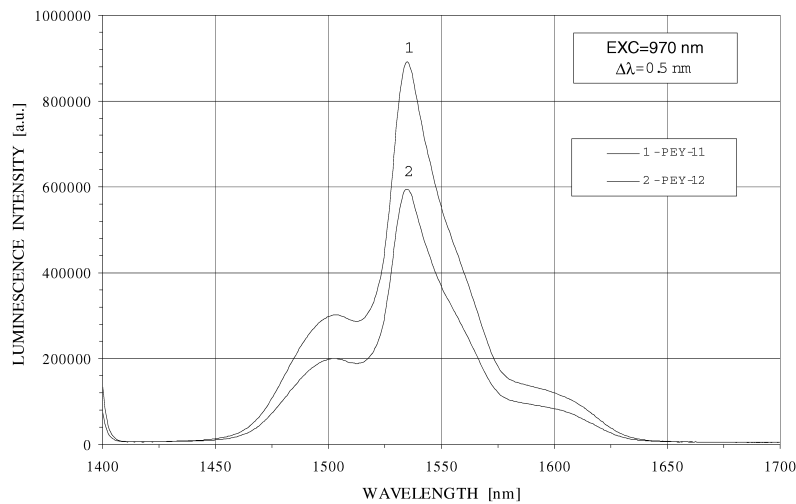


Fig. 6. Luminescence spectra of the PEY-11 (Yb³⁺ + Er³⁺) and PEY-12 (Yb³⁺ + Er³⁺ + Cr³⁺) glasses.

shows the spectra of the absorption coefficient for Yb^{3+} , Er^{3+} , and Cr^{3+} doped PEY-12 and PEYPb-02 glasses and for PEY-11 and PEYPb-01 with no Cr^{3+} ions. The spectra are given for the wavelength range of 200 to 1100 nm. Absorptions were only observed within the visible and IR ranges for the samples doped with active ions.

Investigations on the spectroscopic properties were carried out for all glass samples doped with Yb^{3+} , Er^{3+} , and Cr^{3+} .

The measurements of the luminescence spectra have been performed with a H20 Jobin-Yvon monochromator (focal length 200 mm). For excitation a laser diode emitting at 970 nm was used. The luminescence was registered by means of a Lock-in (Stanford Research SR510) system with a thermoelectrically cooled InGaAs detector. The luminescence spectra are presented in Figs. 5–7.

The measurements of the lifetime of the ions in the upper laser level (${}^4\text{I}_{13/2}$) of the samples doped with Er^{3+} and Yb^{3+} were made by the direct method with pulse excitation. The crystal was excited with a radiation pulse significantly shorter than the lifetime τ of the excited level. After excitation the fluorescence decay can be observed. As a source of the exciting pulses of wavelength 970 nm (excitation of Er^{3+} and Yb^{3+} ions) a Polaroid 4300 laser diode was used. The laser was supplied from a power supply SDL800, controlled by a pulse generator and generated pulses of about 8 μs duration at a frequency of about 0.66 kHz. In the detection channel, perpendicular to the excitation channel, a germanium photodiode was used

and the fluorescence decay was registered with a digital oscilloscope LeCROY 9350AM (500 MHz).

Fig. 8 presents the fluorescence decay of the phosphate glass samples.

The fluorescence intensity I versus the time t was approximated numerically by the following function

$$I = I_0 \exp\left(-\frac{t}{\tau}\right)$$

where I_0 is the initial intensity and τ the fluorescence decay time.

The fluorescence decay times of the examined samples are listed in Tables 2 and 3.

6. Conclusions

The conditions of growing YAG:Er^{3+} and YAG:Er^{3+} , Yb^{3+} monocrystals of various concentrations, devoted to lasers generating eyesafe radiation, were determined. The investigation of the optical and spectroscopic properties of the obtained crystals showed their good optical quality.

Due to the advantageous spectroscopic parameters of YAG:Er^{3+} and YAG:Er^{3+} , Yb^{3+} crystals and their high thermal and mechanical stability characteristic for garnets, those crystals can be used in laser technology as active materials of lasers generating eyesafe radiation.

The conditions of synthesis of various phosphate glasses doped with erbium, ytterbium, and chromium, devoted to laser systems generating eyesafe radiation, were also

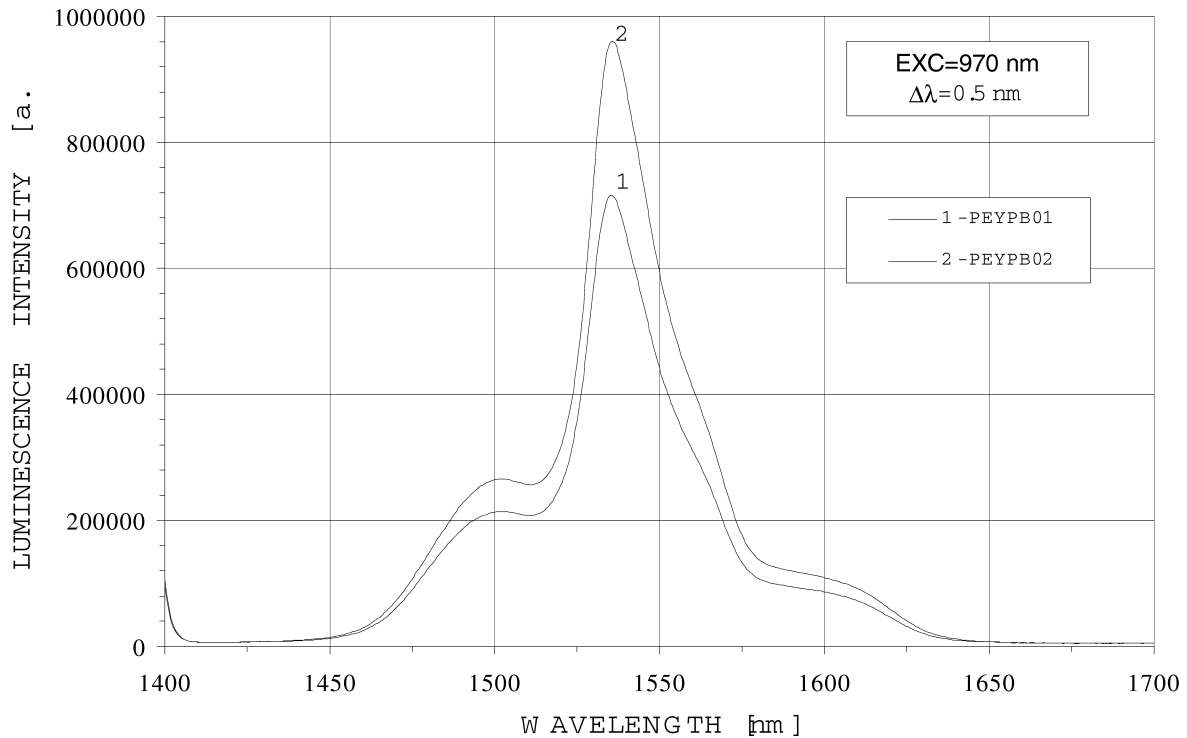


Fig. 7. Luminescence spectra of the PEYPb-01 ($\text{Yb}^{3+} + \text{Er}^{3+}$) and PEYPb-02 ($\text{Yb}^{3+} + \text{Er}^{3+} + \text{Cr}^{3+}$) glasses.

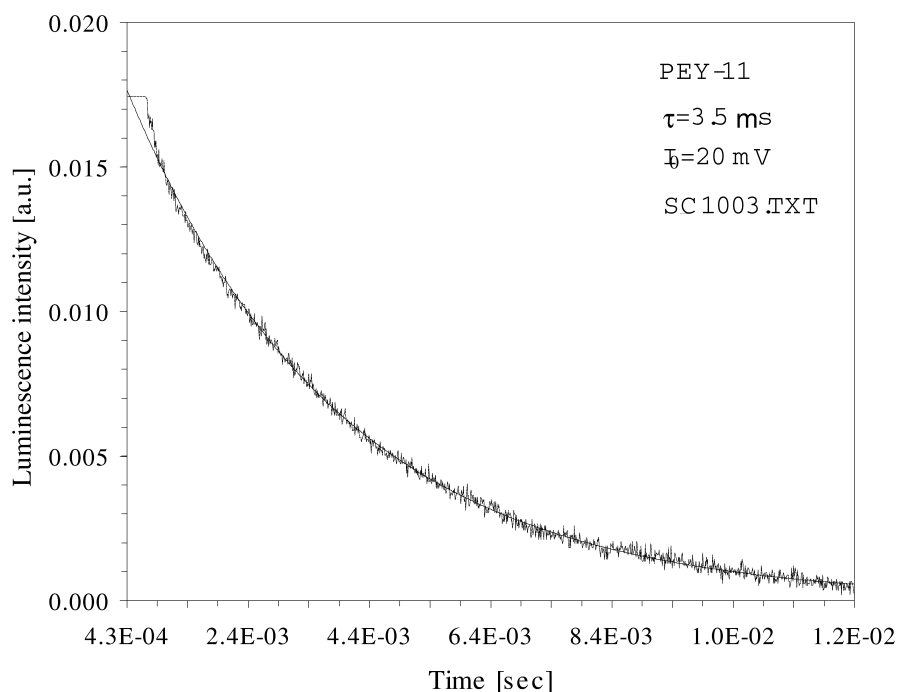


Fig. 8. Fluorescence decay in the PEY-11 phosphate glass.

Table 2

The fluorescence decay times (level $^4I_{13/2}$) of the investigated YAG:Er³⁺ and YAG:Er³⁺, Yb³⁺ crystals

Crystal	Fluorescence decay time (ms)
YAG:Er ³⁺ (1.5% Er ³⁺)	5.6±0.1
YAG:Er ³⁺ , Yb ³⁺ (0.9% Er ³⁺ , 9% Yb ³⁺).	4.3±0.1
YAG:Er ³⁺ , Yb ³⁺ (0.5% Er ³⁺ , 5% Yb ³⁺)	3.5±0.1

given. Investigations carried out on the thermal, optical, and spectroscopic properties of the obtained glasses showed their good quality, ensuring the possibility of their application in laser systems.

The characteristic absorption bands do not depend on the chemical constitution of the glass matrix (examined matrices were characterised by high contents of P₂O₅). The presence of a weak absorption band near 2.22 μm resulting

Table 3

The fluorescence decay times of the level $^4I_{13/2}$ in the examined samples of erbium glass

Glass type	Fluorescence decay time (ms)
PEY-01	4.2±0.1
PEY-02	3.8±0.1
PEY-11	3.5±0.1
PEY-12	3.4±0.1
PEYPb-01	3.7±0.1
PEYPb-02	3.5±0.1

from the existence of OH⁻ groups in the glass structure was stated.

The obtained phosphate glasses are characterised by an advantageously low coefficient of thermal expansion important for resistance to thermal shock, especially when they are applied as rods for lamp pumped lasers.

Acknowledgements

The investigations were made within the frame of grant no. 160/T00/97/13 financed by the State Committee for Scientific Research.

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