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Nd^{3+}-, Er^{3+}- and Pr^{3+}-doped fluoride glasses for laser applications

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Abstract

Great progress has been observed in recent years in the development of Nd^{3+}-, Er^{3+}- and Pr^{3+}-doped fluoride glasses appropriate for fibre lasers, upconversion laser systems, and amplifiers operating at 1064 and 1550 nm. A series of fluoride glasses doped with different concentrations of Nd^{3+}, Er^{3+} and Pr^{3+} ions have been prepared. The room temperature fluorescence spectra of these glasses under various excitation wavelengths have been investigated. Fluorescence lifetimes have been measured for the most interesting transitions.

Keywords: Fluoride glasses; Rare earth; Fluorescence; Lasers

1. Introduction

Great interest in fluoride Nd^{3+}-, Er^{3+}-, Pr^{3+}-doped glasses observed in recent years is first of all due to their possible applications as active media for fibre lasers, optical amplifiers, and laser systems of the 'up-conversion' type [1,2].

Fluoride glasses, in comparison with typical silica glasses used in fibre-optic telecommunication, are characterised by low attenuation of radiation in a significantly wider range of wavelengths i.e., from 0.2 to 7 μm [3]. The different energetic structure of those glasses and low energies of phonons [4–6] in comparison with commonly used silica, silicate, and phosphate glasses make a significant number of quantum transitions of high efficiency possible when glasses are doped with rare earth ions, especially within the range of longer wavelengths. It is evident from the literature data [7,8] that many of those radiant transitions were observed only in glasses based on pure fluorides.

Fluoride glasses doped with rare earth ions can be widely applied in telecommunication, optoelectronics, medicine, and environmental protection. In particular, the possible applications of these glasses in telecommunication testifies the amplification of radiation obtained for wavelengths of 0.8 μm [9,10], 1.06 μm, 1.3 μm [11–15], and 1.54 μm [15–17] used in telecommunication windows of minimal attenuation for silica which is the most frequently used fibre as a transmitting medium. A wavelength of 1.3 μm is interesting because until now there was a lack of amplifiers that are quantum efficient enough to be used in the majority of fibre-optic lines already in use.

Fluoride amplifiers for 1.55 μm are considered by some manufacturers as more advantageous because their bands are much wider and plane which is good for application of many amplifiers set in a cascade system or DWDM dense multiplexing that is now extensively developed.

The possibility of optical amplification within the range of wavelength of 2.7 μm [18–20] is promising for performance of a high power source applied to a surgical instrument due to very strong absorption by OH^- ions within this range of wavelengths. In many laboratories in the world, researchers obtained significant experience in the performance of coherent fibre sources of a power of several watts for continuous operation and several kilowatts for pulse operation with no thermal and optical degradation of the fibre. The radiant transitions within visible light, especially within the blue and green spectrum are also possible with the up-conversion process [21–23]. Rare earth dopants can be easily introduced into matrices of these glasses. Their low refractive index, of the order of 1.5, easy mechanical treatment, water- and weak acids resistance are the decisive factors of this material applicability.

The aim of the work carried out was to obtain active fluoride glass of ZBLAN type that is the recommended type of fluoride glass due to its optical properties. Elaboration of synthesis of Nd^{3+}-, Er^{3+}-, Pr^{3+}-doped fluoride glasses is the basis for further searching for other constitutions of this type of glass with new components that enable

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new radiant transitions to be obtained, especially of continuous bands of tuned coherent sources, and of increased quantum efficiency for wavelengths used in practical applications.

2. Synthesis of glasses

As the optimal constitution of fluoride matrix glass, the constitution of a glass based on fluorozirconate of molecular composition of $53ZrF_4+20BaF_2+4LaF_3+3AlF_3+20NaF$ was taken, known as ZBLAN glass. It is the most stable fluoride glass system, resistant to crystallisation during its secondary heating up to softening temperature when glass is pulled as a fibre.

Doping of fluoride glasses with rare earth ions was limited to three compounds: neodymium, erbium, and praseodymium fluorides. Fluoride compounds of the Fluortran® (fibre grade) MERC firm were used for glass synthesis.

Among the raw materials used for the melting process only ZrF_4 is a fusible material, $T_{mel} \cong 600$°C. Other crystals have a melting temperature over 1000°C; BaF_2—1280°C, LaF_3—1493°C, AlF_3—1291°C, NaF—988°C, NdF_3—1410°C, and ErF_3—1380°C. Actually these crystals dissolve slowly in ZrF_4 liquid. Thus, there is a necessity of a long maintenance of a melt at high temperature until all the crystals dissolve. This is also the reason for the higher volatility of ZrF_4 because the pressure of the steam of the particular components, as a function of temperature, are similar. Volatility of ZrF_4 was corrected by adequate addition of this component to the raw material in the amount resulting from molecular composition.

A melting platinic crucible containing the melt was placed inside a melting furnace and heated up to a temperature of 750–800°C and kept at this temperature for 2–3 h. Next, the temperature was slowly lowered down to a casting temperature of glass mass, i.e., to about 600–640°C and this temperature was kept for about 0.5 h in order to make the temperature distribution more uniform. Next, the crucible was taken out from the furnace, its cover was removed and liquid glass was poured into the heated mould that had been taken from another furnace.

For relief of glass stress, the furnace was heated up to a temperature of 290–300°C. After heating and keeping at this temperature for 1 h, the temperature was reduced down to 220–260°C. After casting the sample in a mould, it was placed into a furnace again and underwent an annealing process for about 0.5 h at a temperature of 220–260°C, next it was cooled to room temperature at a rate of 0.3°C/min.

Such a melting process made it possible to obtain the samples of glass in the form of rods of diameter of 10 mm and maximal length of 100 mm. Glasses were characterised by high homogeneity and there were no gaseous and crystalline inclusions inside them.

3. Examination of glass properties

Dilatometric measurements were made that consisted in determination of a coefficient of linear thermal expansion $\alpha = 185 \pm 2 \times 10^{-7}$ K^{-1} for temperatures 20–200°C, transformation temperature $T_g = 259 \pm 5$°C and dilatometric softening point DSP = 282±5°C. Moreover, the refractive index was determined and its value was $n_d = 1.497$.

In order to determine the dependence of the absorption coefficient on wavelength $k(\lambda)$ for the investigated samples, the measurements of transmission as a function of wavelength were performed. Measurements were carried out within the spectral range of 200–1100 nm ($\Delta\lambda = 1$ nm) using a LAMBDA2 PERKIN ELMER spectrophotometer, within the range of 1100–1500 nm ($\Delta\lambda = 1$ nm) using an ACTA MVII BECKMAN spectrophotometer, and within the range of 1500–25 000 nm ($\Delta 1/\lambda = 1$ cm^{-1}) using a Fourier PERKIN ELMER spectrophotometer 1725-X FT–IR.

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

The spectra of the absorption coefficient for Nd^{3+}, Er^{3+}, Pr^{3+}-doped glasses, determined for wavelengths of 200–1100 nm, are shown in Figs. 1–3.

Measurements of luminescence spectra for the samples of fluoride Nd^{3+}, Er^{3+}, and Pr^{3+}-doped glasses have been performed with a H20 JOBIN YVON monochromator (focal length 200 mm). For excitation, the following laser sources were used:

- Diode laser emitting radiation at 810 nm (Nd^{3+}-doped glasses).
- Diode laser emitting radiation at 970 nm (Er^{3+}-doped glasses).
- HeCd laser emitting radiation at 442 nm (Pr^{3+}-doped glasses).

The luminescence was registered by means of a LOCK-IN system (Stanford Research SR510) with a thermoelectrically cooled InGaAs detector. Luminescence spectra are presented in Figs. 4–6.

Measurements of lifetimes at the upper laser level for the samples of ZBLAN (1%, 2%, and 3% NdF_3) and ZBLAN (1% ErF_3 and 2% ErF_3) were made by the direct method with pulse excitation. The investigated medium was excited with radiation pulse duration significantly

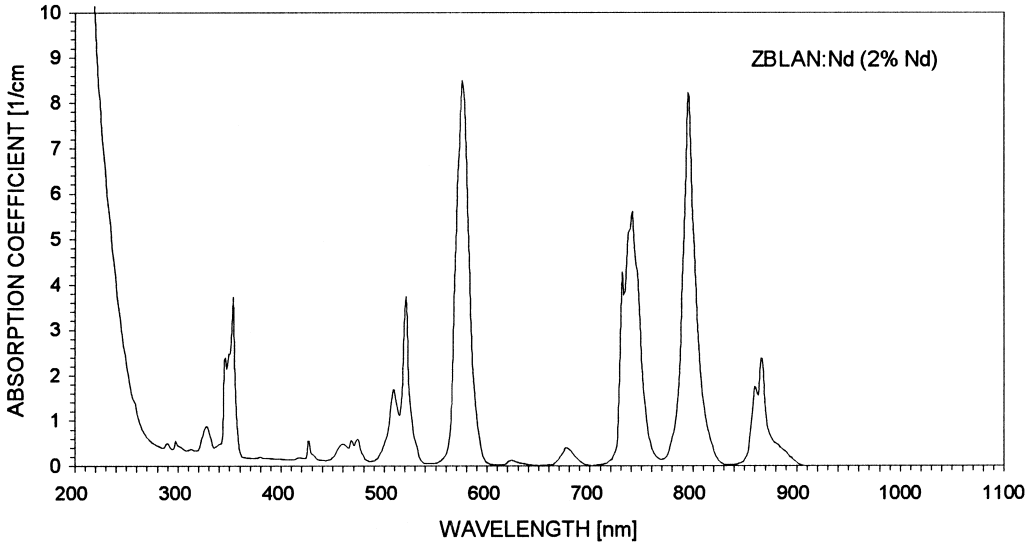

Fig. 1. Absorption spectra of neodymium-doped ZBLAN glass.

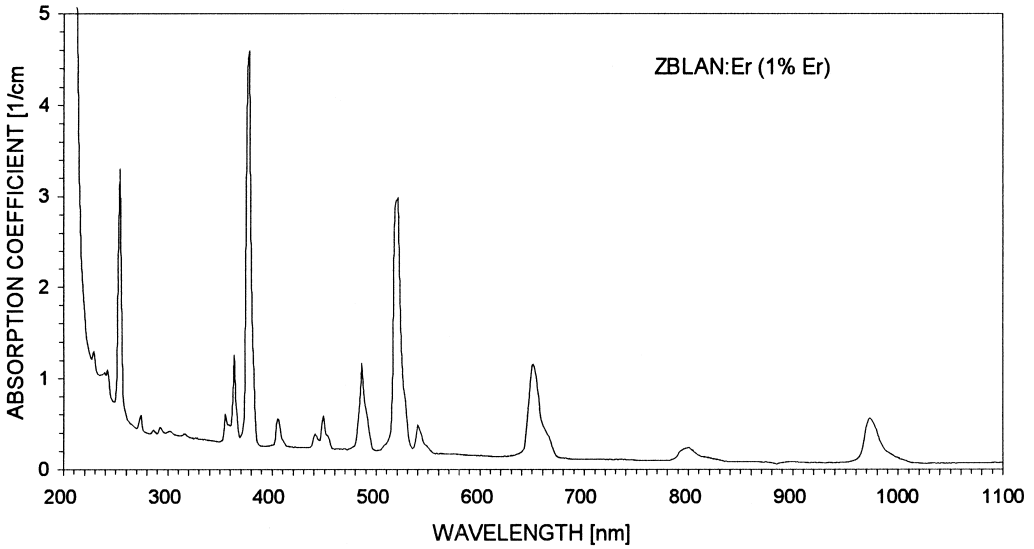

Fig. 2. Absorption spectra of erbium-doped ZBLAN glass.

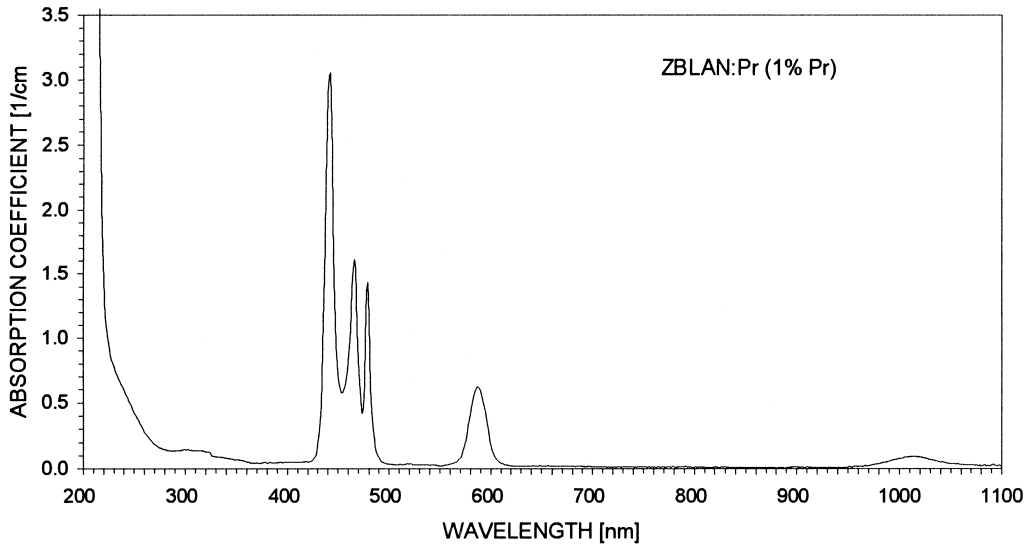

Fig. 3. Absorption spectra of praseodymium-doped ZBLAN glass.

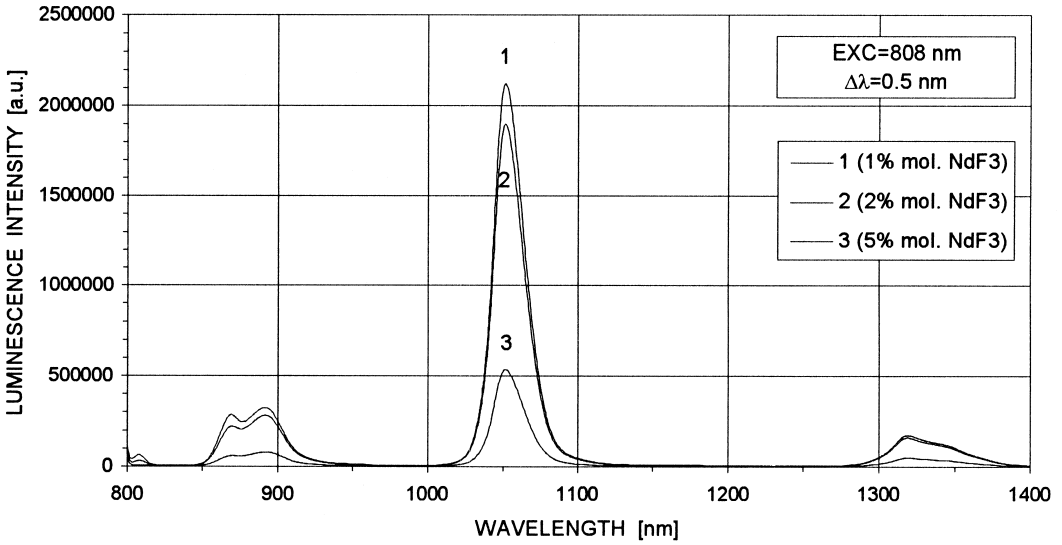

Fig. 4. Luminescence spectra of neodymium-doped ZBLAN glasses.

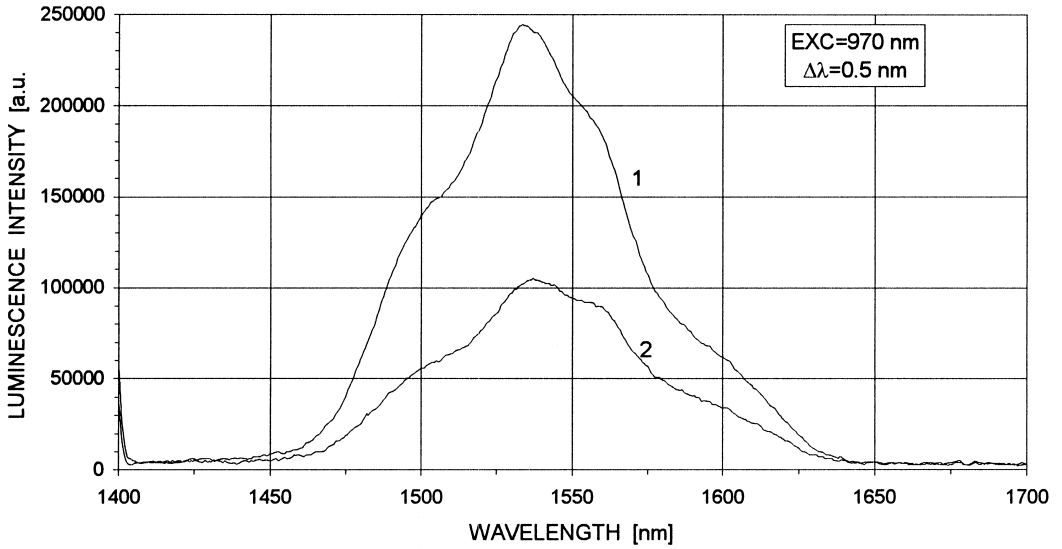

Fig. 5. Luminescence spectra of erbium-doped ZBLAN glasses.

shorter than the lifetime τ at the excited level. After excitation, a population level decay occurs, the evidence of which is fluorescence decay that can be observed.

A source of diagnostic pulses of wavelength 808 nm (excitation of Nd^{3+} ions) was a SDL2432 diode laser and the pulses of the 970-nm wavelengths (excitation of Er^{3+} ions) was a diode laser Polaroid 4300. The lasers were supplied from a power supply SDL800, controlled by a pulse generator and generated pulses of about 8-μs duration at a frequency about 0.66 kHz.

In the detection channel, perpendicular to the excitation channel, a silica and germanium photodiode was used and the fluorescence decay was registered with a digital oscilloscope LeCROY 9350AM (500 MHz).

Typical temporal courses in the excitation and emission channels were registered by means of the oscilloscope shown in Fig. 7. The shape of an excitation pulse is presented in Fig. 8. As it can be seen in Fig. 8, pulse decay time does not exceed 1 μs, so the condition that the diagnostic pulse decay time was significantly shorter than the lifetime τ on the excitation level was fulfilled.

Fig. 9 presents the temporal course of fluorescence decay in the ZBLAN+2% ErF_3 glass sample.

The obtained results of the fluorescence intensity (I) versus the time (t) were approximated numerically by the function:

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

where I_0 is the initial intensity, and τ is the time-constant.

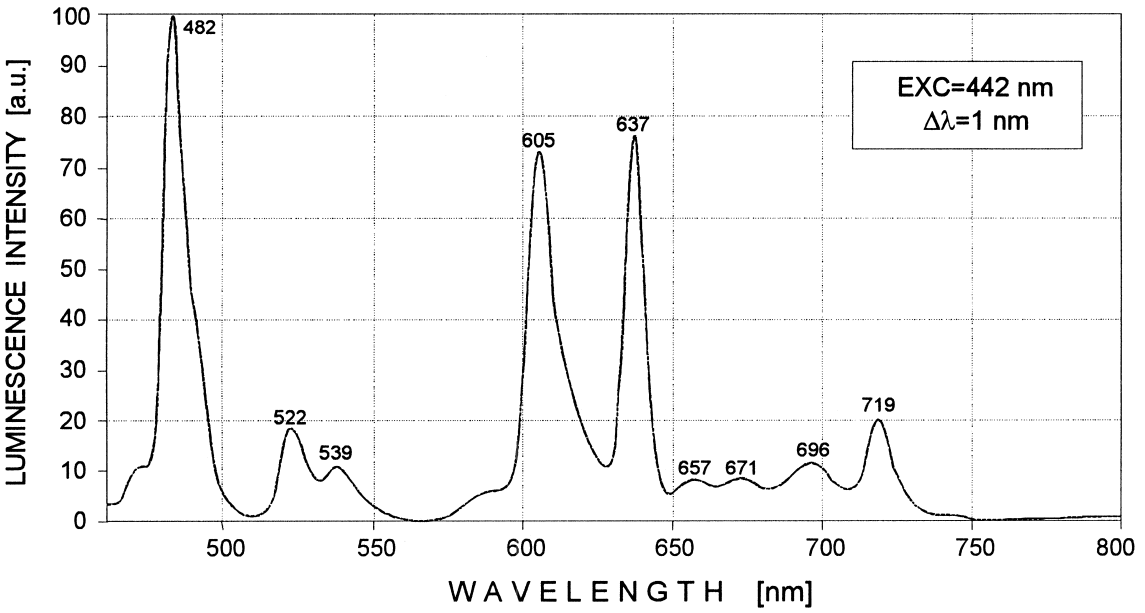

Fig. 6. Luminescence spectra of praseodymium-doped ZBLAN glass.

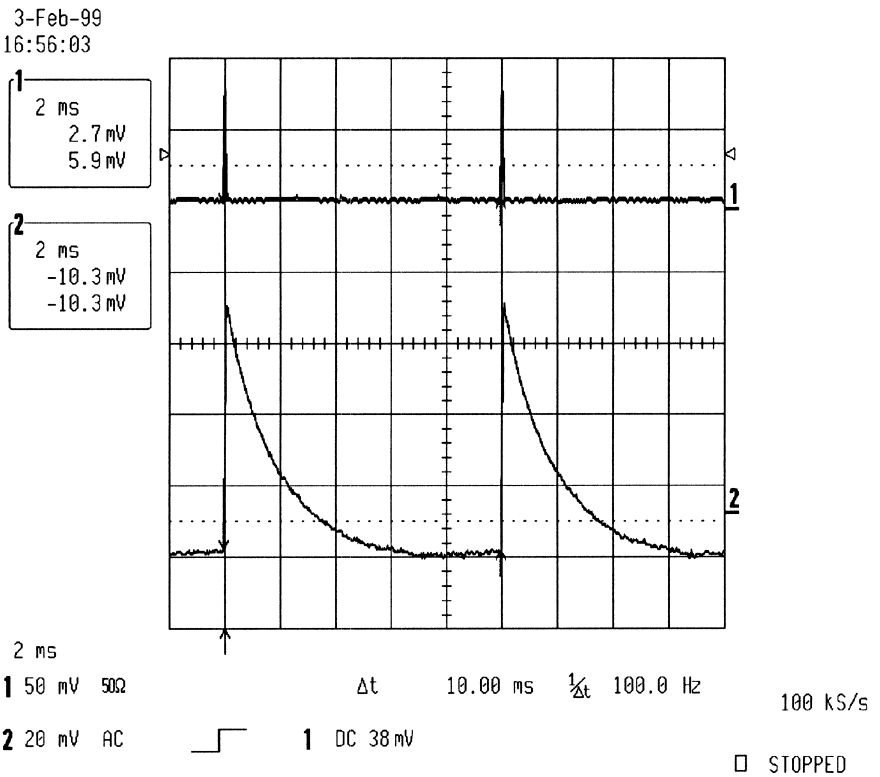

Fig. 7. Typical temporal courses in the excitation channel (1) and emission channel (2) registered by means of a LeCROY 9350AM oscilloscope.

The fluorescence decay times of Nd^{3+} and Er^{3+}-doped glasses are presented in Table 1.

4. Conclusions

The conditions of synthesis of fluoride glasses doped with neodymium, praseodymium, and erbium, devoted to laser applications, were defined. These are the most promising dopants as far as practical application is concerned. With a neodymium-doped matrix, a laser action can be achieved or amplification of radiation at 1.06 μm wavelength. Praseodymium is a basic dopant used for light amplification in a fibre in a telecommunication window of

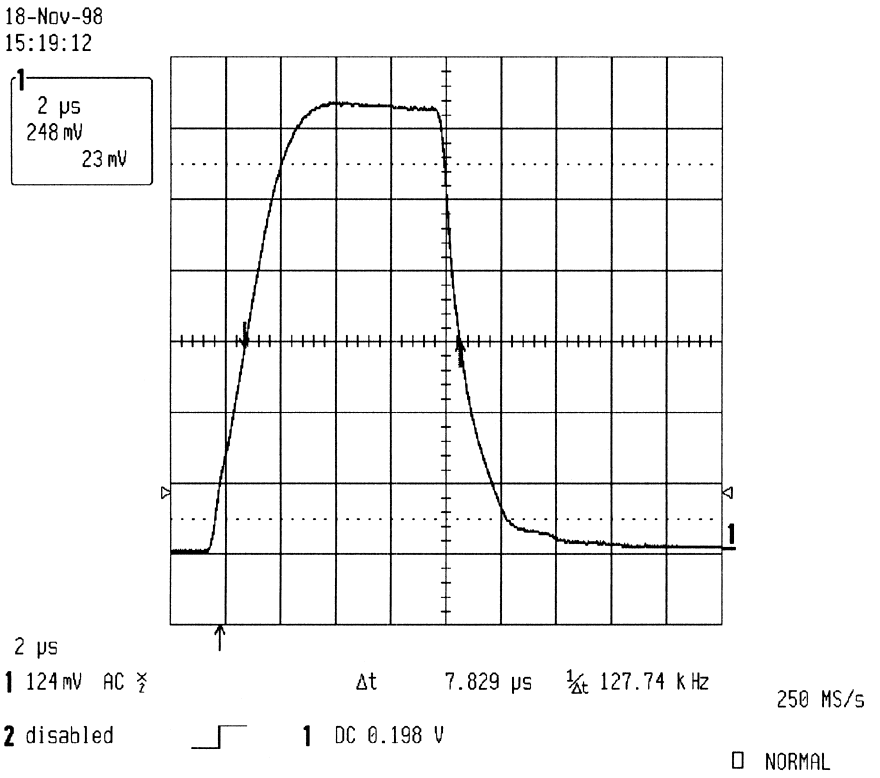

Fig. 8. Oscillogram of temporal course of a pulse exciting the active medium examined.

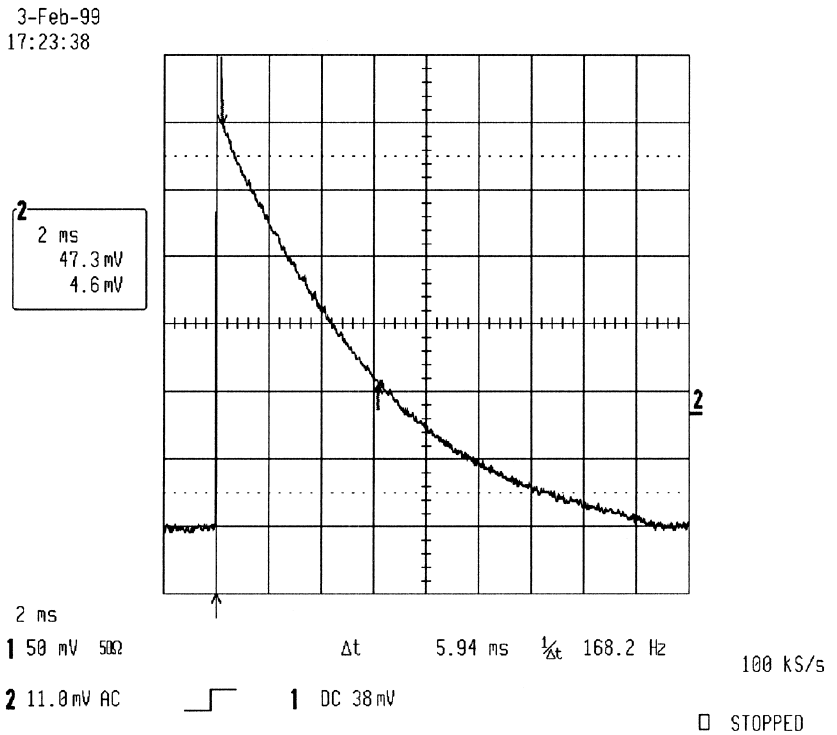

Fig. 9. Oscillogram of the temporal course of fluorescence decay in the ZBLAN+2% ErF_3 glass sample.

Table 1
The fluorescence decay times of neodymium ($^4F_{3/2}$ level) and erbium ($^4I_{13/2}$ level)-doped ZBLAN glasses

Glass type	Fluorescence decay
ZBLAN+1 mol.% NdF_3	482±5 μs
ZBLAN+2 mol.% NdF_3	387±5 μs
ZBLAN+5 mol.% NdF_3	181±5 μs
ZBLAN+1 mol.% ErF_3	6.5±0.1 ms
ZBLAN+2 mol.% ErF_3	6.7±0.1 ms

1.3 μm. Erbium fluoride glass is an ideal material for a laser system generating radiation of a wavelength of about 2.8 μm. An optical fibre made of such a material can be a generator or an amplifier of optical signal in a surgical instrument. Erbium-doped fluoride amplifiers for wavelength of 1.55 μm are more and more popular due to their plane transmission characteristics. Moreover, these dopants can be used for up-conversion effect realisation and laser action achievement within the range of visible light.

The investigations carried out on the thermal, optical, and spectroscopic properties of the prepared Nd^{3+}, Er^{3+}, Pr^{3+} fluoride glasses showed their good quality for application in laser systems.

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