

# Absorption and luminescence properties of Cr<sup>4+</sup>-doped silica fibres

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**Abstract.** The absorption and luminescence spectra of silica fibres doped with chromium and various dopants are studied. Fibres doped with aluminium and gallium exhibit a broad (300 nm) luminescence band of Cr<sup>4+</sup> ions at 1100 nm at room temperature. The quantum yield of luminescence is estimated to be 10<sup>-4</sup> – 10<sup>-5</sup>.

**Keywords:** optical fibres, Cr<sup>4+</sup> ion, luminescence.

## 1. Introduction

The development of silica-fibre broadband tunable near-IR (1.3 and 1.55  $\mu\text{m}$ ) radiation sources is one of the most important problems of fibre optics. This stimulated recent interest in chromium-doped glasses [1–4]. According to the data from the literature, the Cr<sup>4+</sup> ions have in different glasses a broad absorption band in the visible and near-IR regions, as well as a broad luminescence band in the near-IR region containing the wavelengths 1.3 and 1.55  $\mu\text{m}$ . Therefore, Cr<sup>4+</sup>-doped silica glasses are promising materials for fabrication of tunable fibre lasers and amplifiers, as well as ultrashort-pulse lasers with broadband pumping. The spectral properties of Cr<sup>4+</sup> ions in doped silica glasses have been studied only in a few papers [1–4]. It is necessary to continue the study of effects of various dopants in the glass and of their concentration on the degree of oxidation of chromium and the luminescent properties of Cr<sup>4+</sup> ions, especially in the case of high-temperature technological regimes, which are used for the production of optical fibres by the method of modified chemical vapour deposition (MCVD).

In this paper, we studied the absorption and luminescence spectra of chromium ions in fibres with germano-alumino- and gallium-silicate cores.

## 2. Methods for preparation of samples and their parameters

Glass preforms for fibres were fabricated by the MCVD method. The main Ge and Al dopants forming the refractive-index profile were doped into glass by oxidising the corresponding chlorides in vapour, while Ga and other elements (Mg and Cr) were doped by impregnating a porous MCVD glass layer with solutions of their salts followed by the evaporation of the solvent and melting the porous layer. The concentrations of GeO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in the fibre core were determined from the refractive-index profile of the preform. The content of Ga, Mg, and Cr is presented in gram-ions of the corresponding metals per 100 mL of solution (Table 1). Few-mode fibres were drawn from glass preforms (the difference between the refractive indices of the fibre core and cladding was  $\Delta n \sim 0.01 - 0.02$  and the cut-off wavelength was  $\lambda_c \sim 4000$  nm).

**Table 1.** Molar concentrations of germanium and aluminium oxides, and the concentrations (in gram-ion per 100 mL) of gallium ions in the fibre core glass and of Mg and Cr in solutions for impregnating porous glasses in samples under study.

| Fibre | GeO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Ga   | Mg   | Cr     |
|-------|------------------|--------------------------------|------|------|--------|
| AJ-25 | 9                | –                              | –    | 0.12 | 0.13   |
| FF-1  | –                | 8.5                            | –    | –    | 0.0098 |
| FF-3  | –                | –                              | 1.35 | –    | 0.0078 |
| FF-4  | –                | 7.5                            | –    | 0.08 | 0.0068 |

## 3. Methods and results of absorption and luminescence measurements

The optical losses in fibres were several tens of decibels per metre, which prevented the accurate measurements of the absorption spectra by a standard method of comparing the intensities of emission coming from the short and long fibre pieces. For this reason, (after a preliminary estimate of losses and the luminescence spectrum) the segments of a single-mode germanosilicate fibre with low losses ( $\Delta n \sim 0.01$ ,  $\lambda_c \sim 1200$  nm) several metres in length were spliced from two sides to the short segment of the fibre under study. The length of the fibre segment was chosen to obtain the maximum luminescence intensity at the fibre output upon excitation at 650 nm. This length was from 15 to 40 cm for different fibres.

Then, we measured the optical loss spectra for such fibres in the range from 500 to 1800 nm using a setup that

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included a KGM-70 incandescent lamp and an MDR-23 monochromator. A signal at the fibre output was measured with an FD-24K silicon or an FD-5G germanium photodiode and was detected with an NF Electronic, model 9610 lock-in amplifier. The signal attenuation was mainly determined by losses in fibres. Because the parameters of spliced fibres were noticeably different, the splicing losses were rather large (up to 1 dB), however, the weak spectral dependence of these losses allowed us to take easily their contribution into account. In addition, we measured the intensity of scattering through the side surface of the fibre close to the output end upon excitation of fibres by a cw Kr<sup>+</sup> laser (Spectra Physics, model 165) at 476, 520, 568, 647, and 676 nm (the radiation power in the fibre was from 1 to 50 mW). The measurements showed that the scattering losses did not exceed 0.1 dB m<sup>-1</sup> for all fibres and were negligible compared to total losses, which, therefore, are mainly determined by absorption.

Fig. 1 shows the absorption spectra for series FF fibres with the alumino-silicate core. As in papers [1, 2], the absorption spectra weakly depended on temperature. Fig. 2 shows the absorption spectrum of the FF-1 fibre at 77 K, which is decomposed into five Gaussian components.

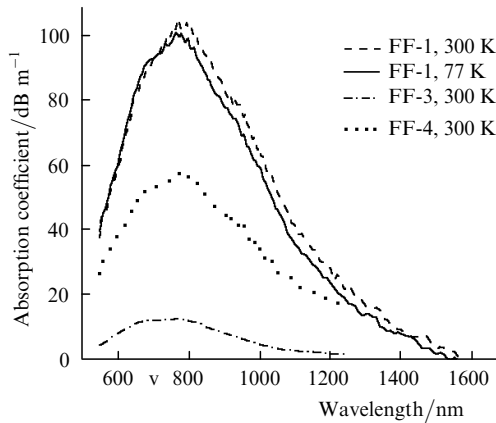


Figure 1. Absorption spectra of FF series fibres.

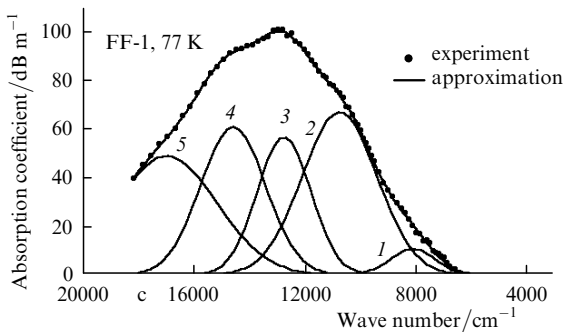


Figure 2. Absorption spectrum of the FF-1 fibre (each second point is shown) and its decomposition into five Gaussian components).

The luminescence spectra were recorded upon excitation by a Kr<sup>+</sup> laser (power in the fibre was  $\sim 10$  mW) and by a Nd:YAG laser at 1064 nm (power in the fibre was  $\sim 100$  mW). The spectrum of emission coming from the fibre was analysed with an MDR-6U double monochromator and, upon excitation at 1064 nm, using an additional

dielectric mirror reflecting laser radiation. The luminescence intensity was measured with a germanium photodiode using a lock-in amplifier. The absorption and luminescence spectra at 77 K were measured by placing fibres in a Dewar vessel with liquid nitrogen.

The luminescence intensity depended on the glass composition and temperature much stronger than absorption. Luminescence was observed for all fibres at 77 K upon excitation at 568, 647, and 676 nm. The most intense luminescence was observed for FF-1, FF-3, and FF-4 fibres, its intensity being sufficient for recording the spectra at 77 and 300 K. In addition, we observed luminescence of the FF-1 fibre upon excitation by a Ti:Al<sub>2</sub>O<sub>3</sub> laser at 740, 765, 781, 801, and 803 nm (the power in the fibre was  $\sim 10$  mW). We failed to detect luminescence upon excitation of fibres at 476, 530, and 1064 nm.

In all cases, we observed luminescence bands of the same shape of width 300 nm with a maximum at 1100 nm. Fig. 3 shows the luminescence spectra of the FF-1 fibre at 77 and 300 K. The narrow lines are laser lines reflected in the second order of the monochromator grating (1294 nm). Upon excitation at 647 nm, the luminescence band was somewhat broader than upon excitation at 765 nm.

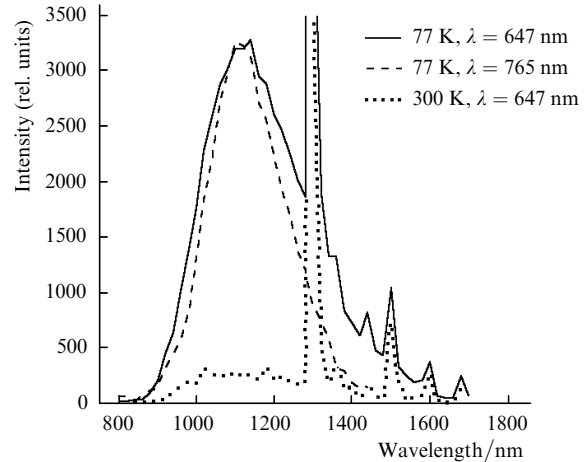


Figure 3. Luminescence spectra of the FF-1 fibre excited at 647 nm at 77 and 300 K and at 765 nm at 77 K. The spectra excited at 647 nm are recorded on the same scale.

Table 2 presents the quantum yields of luminescence at 77 and 300 K, which were calculated taking into account the photodetector sensitivity, the radiation losses in the monochromator, and the numerical aperture of fibres. The relative accuracy of the data presented in Table 2 is 10%, the error of the estimate of the absolute value of  $\eta$  can be twofold. The quantum yield of luminescence at 77 K was independent, within the measurement accuracy, of the excitation wavelength varied in the range from 568 to 676 nm for all fibres and from 568 to 823 nm for the FF-1 fibre.

Table 2. Quantum yield of luminescence  $\eta$ .

| Fiber | $T = 77$ K          | $T = 300$ K         |
|-------|---------------------|---------------------|
| FF-1  | $1.9 \cdot 10^{-4}$ | $2.6 \cdot 10^{-5}$ |
| FF-3  | $3.2 \cdot 10^{-4}$ | $2.2 \cdot 10^{-5}$ |
| FF-4  | $5.3 \cdot 10^{-4}$ | $3.3 \cdot 10^{-5}$ |

## 4. Discussion of results

The measurements of scattering showed that the scattering losses in all fibres studied are negligible compared to absorption. According to the data presented in papers [1–4], the absorption spectrum of fibres with aluminosilicate and gallium-silicate cores is determined by the  $\text{Cr}^{4+}$  ions. The shape of the spectrum is well approximated by a sum of five Gaussians (Fig. 2, Table 3). A lower number of components cannot provide a satisfactory fitting.

**Table 3.** Parameters of Gaussian components in the decomposition of the absorption spectrum and their identification.

| Peak number | Centre/ $\text{cm}^{-1}$ | Width/ $\text{cm}^{-1}$ | Transition          |
|-------------|--------------------------|-------------------------|---------------------|
| 1           | 8123.2                   | 1600                    | ${}^3T_2 - {}^3A_2$ |
| 2           | 10755                    | 2690                    | ${}^3T_2 - {}^3A_2$ |
| 3           | 12757                    | 1927                    | ${}^3T_1 - {}^3A_2$ |
| 4           | 14585                    | 2337                    | ${}^3T_1 - {}^3A_2$ |
| 5           | 16977                    | 3606                    | ${}^3T_1 - {}^3A_2$ |

The  $\text{Cr}^{4+}$  ion has a small ion radius and prefers the tetrahedral environment. Using the Tanabe–Sugano diagrams for an ion with the electronic configuration  $3d^2$  in the tetrahedral environment, we can assign the absorption spectrum to the  ${}^3A_2 - {}^3T_1$  and  ${}^3A_2 - {}^3T_2$  transitions [5–7]. Each of the  ${}^3T_1$ ,  ${}^3T_2$  levels is triply degenerate in the symmetry  $T_d$  and is split when the symmetry decreases, which explains the bands observed.

The parameters of the bands and their assignment to certain transitions are presented in Table 3. One can see from this table that luminescence is observed upon excitation of the  ${}^3T_1$  level. The increase in the luminescence quenching (approximately by a factor of ten) with increasing temperature from 77 to 300 K can be explained by multiphonon relaxation, which occurs more efficiently in glasses than in crystals because the phonon spectrum of glasses is broader. In addition, the closely spaced levels  ${}^3T_1$  and  ${}^1E$  are mixed due to the spin–orbit interaction, which is also facilitated by the splitting of the  ${}^3T_1$  level. The possibility of this effect was discussed in paper [4]. In this case, the luminescence spectrum should also depend on temperature.

The authors of papers [1, 2] also observed luminescence of aluminosilicate fibres at 77 K. They obtained the loss spectra that had the shape and position very close to those observed in our paper. Some difference in the spectra can be attributed to the technology of fibre fabrication, namely, by the fact that aluminium was introduced by impregnation in papers [1, 2], whereas in our sample it was doped by the MCVD method. The difference in the luminescent parameters was more significant. The authors of papers [1, 2] reported a band of a complicated shape at  $\sim 1250$  nm, which was observed only at 77 K and was assigned by the authors to the  ${}^3T_2 - {}^3A_2$  transition. We observed a band of symmetrical shape of width 300 nm with a maximum at 1100 nm at 77 and 300 K upon excitation of the  ${}^3T_1$  level. Upon excitation of the  ${}^3T_2$  level at 1064 nm, no luminescence was observed.

In the case of the germanosilicate AJ-25 fibre co-doped with magnesium and chromium, it is difficult to assign absorption in the visible region to chromium of a certain degree of oxidation because absorption caused by the  $\text{Cr}^{3+}$  ions can interfere. The increase in absorption observed in the short-wavelength region beginning from 500 nm sug-

gests that the  $\text{Cr}^{3+}$  ions can be present in the fibre [3]. The data on stabilisation of chromium ions in the degree of oxidation +3 by germanium are presented in paper [2]. The luminescence band that we observed at 77 K is similar in its shape, width and position to the luminescence band of an aluminosilicate fibre doped with chromium, which indicates the presence of chromium in the degree of oxidation +4. Thus, we conclude that doping of germanosilicate fibre with magnesium at least partially stabilises chromium in the degree of oxidation +4.

## 5. Conclusions

We have observed for the first time, to our knowledge, the luminescence of  $\text{Cr}^{4+}$  ions in aluminosilicate and gallium-silicate fibres at room temperature. The fibres were manufactured by the MCVD method, and chromium and magnesium were doped by impregnation. The luminescence band has a maximum at 1100 nm and a width of 300 nm. Luminescence was observed upon optical excitation in the range from 568 to 823 nm. The quantum yield of luminescence was independent of the excitation wavelength within the measurement error and was  $\sim 10^{-5}$  at 300 K and  $10^{-4}$  at 77 K.

The doping with magnesium resulted in the increase in the quantum yield of luminescence in an aluminosilicate fibre and caused a partial stabilisation of chromium ions in the degree of oxidation +4 in a germanosilicate fibre. The spectral range of pumping corresponds to excitation of the  ${}^3T_1$  level of  $\text{Cr}^{4+}$  ions in the distorted tetrahedral environment.

Therefore, despite the low quantum yield of luminescence, we have obtained the promising results that stimulate further studies aimed at the development of broadband chromium-doped silica fibre lasers emitting in the near-IR region.

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