

# Sulphur-doped silica fibres

V.I. Gerasimova, A.O. Rybaltovskii, P.V. Chernov, V.M. Mashinsky,  
O.D. Sazhin, O.I. Medvedkov, A.A. Rybaltovskii, R.R. Khrapko

**Abstract.** An optical fibre with low optical losses is manufactured from a sulphur-doped quartz glass. Optical absorption spectra are measured for various parts of the fibre core. Most of the bands of these spectra are assigned to oxygen-deficient centres and colour centres containing sulphur atoms. The photosensitivity of glasses exposed to laser radiation at wavelengths of 193 and 244 nm is investigated to estimate the possibility of their application for producing photorefracting devices. A Bragg grating of the refractive index with  $\Delta n = 7.8 \times 10^{-4}$  is written in a sulphur-doped silica fibre.

**Keywords:** quartz glass, colour centres, photoionisation, optical absorption, single-mode fibre, Bragg grating of the refractive index.

## 1. Introduction

A typical optical fibre is a fused silica waveguide consisting of a core and a cladding with refractive indices  $n_c$  and  $n_{cl}$ , respectively. The required difference in the refractive indices  $\Delta n = n_c - n_{cl}$  is usually attained by doping the silica fibre core with impurities. Silicon is replaced by an element with a larger number of electrons, such as  $Ti^{4+}$ ,  $Ge^{4+}$ ,  $Sn^{4+}$ ,  $Sb^{3+}$ , or with a larger polarisability,  $P^{5+}$ . Doping with fluorine reduces the refractive index of glass and increases its transmission in the UV region; therefore, doping the fibre core with fluorine increases  $\Delta n$ . Chalcogenides can also potentially replace oxygen. Sulphur is a new and unusual dopant for fused silica. In this paper, we describe the synthesis of workpieces and production of an optical fibre with the sulphur-doped silica core, present its characteristics, and briefly review spectroscopic investigations of colour centres, which are produced during the synthesis of workpieces for fibre pulling.

In our opinion, a search for new dopants is one of the most efficient ways to increase the glass photosensitivity. Optical fibres based on glasses with a high photosensitivity are currently widely used as media for writing refractive-

index gratings in them by UV radiation. Germanosilicate and phosphorosilicate (saturated with  $H_2$  and  $D_2$ ) fibres with an induced change in the refractive index  $\Delta n_{ind} = 10^{-4} - 10^{-3}$  exhibit the best results [1]. Additional doping of germanosilicate fibres with nitrogen [2] or their impregnation in a hydrogen atmosphere and a preexposure [3, 4] enhance their photosensitivity, providing  $\Delta n_{ind} > 10^{-3}$ . Therefore, the aim of our study was also to investigate the photosensitivity of quartz glasses doped with sulphur.

## 2. Samples and experimental technique

Spectroscopic studies were performed using preforms for drawing fibres with a core made of sulphur-doped quartz glass. The preforms were synthesised by the plasmochemical SPCVD method [5]. The sulphur-doped glass was produced by adding  $SiO_2$  to a mixture of  $SiCl_4$  and  $O_2$  and was formed during deposition at  $T = 1200^\circ C$ . A decrease in the oxygen content in the gas mixture resulted in an increased sulphur concentration in the deposited glass (Table 1). After the deposition was completed, the support tube collapsed into a rod by heating it up to  $2000^\circ C$  with an external burner. During this procedure, a dry oxygen atmosphere was maintained inside the tube, and chemical transformations occurred in the near-axial deposited layers, which resulted in the formation of a central dip in the refractive-index profile due to diffusion of impurities and a transformation of defects around this dip.

The experimental samples were disks 1 mm thick cut normally to the preform axis. The region doped with sulphur was shaped as a ring with dimensions depending on the disk type (Table 1). The radial absorption distributions were measured with a spatial resolution of 0.13 mm. The absorption spectra were recorded in the range of 190–600 nm at room temperature using a DDS-30 deuterium lamp and an incandescent lamp, an MDR-6

**Table 1.** Parameters of fibre workpieces with a sulphur-doped silica core.

Sample number	Sulphur weight concentration (%)	Chlorine weight concentration (%)	Size of the doped region/mm		Workpiece tube-to-rod collapse conditions
			$d_{min}$	$d_{max}$	
1	0.04	0.2	2.0	2.5	Dry oxygen atmosphere
2	0.5	0.5	0.5	2.0	Without oxygen
3	0.4	2.0	0.5	1.5	Without oxygen

V.I. Gerasimova, A.O. Rybaltovskii, P.V. Chernov D.V. Skobeltsyn  
Institute of Nuclear Physics, M.V. Lomonosov Moscow State University,  
Vorob'evy gory, 119992 Moscow, Russia;

V.M. Mashinsky, O.D. Sazhin, O.I. Medvedkov, A.A. Rybaltovskii,  
R.R. Khrapko Fiber Optics Research Center, A.M. Prokhorov General  
Physics Institute, ul. Vavilova 38, 119991 Moscow, Russia

Received 3 June 2002

Kvantovaya Elektronika 33 (1) 90–94 (2003)

Translated by A.S. Seferov

monochromator, and a FEU-100 photomultiplier. The spectral resolution was 0.2 nm. The photosensitivity of sulphur-doped quartz glasses was measured by irradiating the samples (No. 1) by the second harmonic of a cw Ar laser ( $\lambda = 244$  nm, the irradiation dose was  $1 \text{ kJ cm}^{-2}$ ) and (Nos 2 and 3) by a pulsed ArF laser ( $\lambda = 193$  nm, the irradiation dose was  $1 \text{ kJ cm}^{-2}$ ).

An optical fibre with a core diameter of  $6\text{--}7 \mu\text{m}$  and a total diameter of  $125 \mu\text{m}$  was pulled from sample No. 3 based on a quartz glass with a high weight content of sulphur (0.4%) and chlorine (2%) in the core. The fibre cut-off wavelength is  $\lambda_{\text{cut}} = 0.95 \mu\text{m}$ , and  $\Delta n = 0.006$ . The fibre initial loss spectrum was measured using the fibre cut-back method.

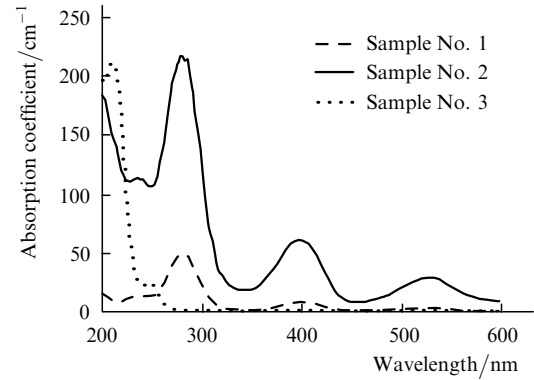
The fibre sensitivity was studied using UV lasers emitting at 193 and 244 nm by writing test refractive-index Bragg gratings on the setup at the Institute of Applied Physics (Lausanne, Switzerland). In the first case, when a Lambda Physik LPX-150 excimer ArF laser (193 nm, the pulse energy density is  $100 \text{ mJ cm}^{-2}$ ) was used, the Bragg gratings were written by using a phase mask, and the parameters of the gratings were measured by an Ando AQ 6317A spectrum analyser at a wavelength of  $1.24 \mu\text{m}$  with a spectral resolution of 0.05 nm. In the second case, the photosensitivity at 244 nm was investigated using the second harmonic of a Spectra-Physics 2045 Ar laser, and the gratings of the refractive index were written by a holographic method using a Lloyd-interferometer-based scheme. The induced refractive index was calculated from the reflectivities of the gratings and shifts of the Bragg reflection wavelength obtained during the irradiation. The length of the test gratings of the refractive index was 5 mm in both cases and allowed its recording to within an accuracy of  $0.5 \times 10^{-4}$ .

### 3. Experimental results and discussion

#### 3.1 Effect of the synthesis conditions

Fig. 1 shows the absorption spectra measured in the regions with the highest sulphur concentration for three samples. Changes in the gas content during the glass production (see Table 1) have led to significant differences in their spectra. The spectrum of sample No. 1 contains four absorption bands peaked at 237, 280, 400, and 525 nm, due to which this sample has a pink-coloured ring. The spectrum of sample No. 2 has the same bands, but their intensity is approximately five times higher. In addition, there is a strong UV wing, which is virtually absent in sample No. 1. Moreover, the ring of sample No. 2 is thinner and, because of a higher intensity of the absorption bands, has a red colour. Sample No. 3 shows no visible colour. Its absorption spectrum is characterised by a strong band at 215 nm and a band at 248 nm; the absorption bands inherent to the spectra of samples Nos 2 and 3 are absent.

We found in our previous works [6, 7] that the bands at 237, 280, 400, and 525 nm belong to ‘sulphur’ colour centres. The absorption bands at 280 and 400 nm have resolved vibrational structures and belong to interstitial  $\text{S}_2$  molecules and  $\text{S}_2^+$  ions, which are weakly bound to the glass network (the  $X^3\Sigma_g^- \rightarrow B^3\Sigma_u^-$  and  $X^2\Pi_{g,r} \rightarrow A^2\Pi_u$  transitions, respectively [6, 7]). The 237-nm band has no vibrational structure probably because of the broadening of the  $B^2\Sigma_g^-$  term, but, nevertheless, it also belongs to the  $\text{S}_2^+$



**Figure 1.** Absorption spectra for sulphur-doped quartz glasses. Measurements were performed in the regions with a maximum sulphur concentration.

molecular ion (the  $X^2\Pi_{g,r} \rightarrow B^2\Sigma_g^-$  transition) [7]. The parameters of these terms are listed in Table 2. The band at 525 nm is most likely related to sulphur, because its radial absorption distribution qualitatively coincides with the radial distributions for the other sulphur bands. However, its behaviour under various external effects does not correlate with the behaviour of any of them [7]. As to the absorption bands at 212 and 248 nm and the UV wing, their behaviour will be discussed below.

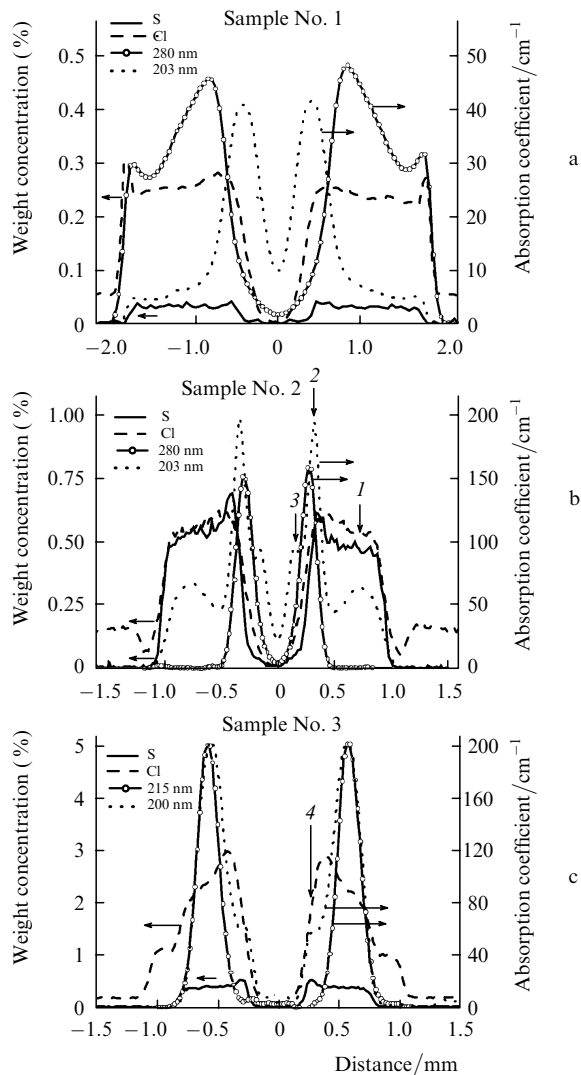
**Table 2.** Parameters of the terms of the  $\text{S}_2$  molecule and the  $\text{S}_2^+$  molecular ion calculated from the experimental data [2, 3].

Type of colour centres	Term	Parameter/ $\text{cm}^{-1}$
$\text{S}_2$ molecule	$X^3\Sigma_g^-$	$\omega_e'' = 707$
		$\omega_e''x_e'' = 1.9$
	$B^3\Sigma_u^-$	$\nu_{00} = 30805$
		$\omega_e' = 434$ $\omega_e'x_e' = 2.5$
$\text{S}_2^+$ molecular ion	$A^2\Pi_u$	$\nu_{00} = 22513$
		$\omega_e' = 536$ $\omega_e'x_e' = 2.45$

Note:  $\nu_{00}$  is the frequency of the 0–0 transition;  $\omega_e''$  and  $\omega_e'$  are vibrational frequencies;  $\omega_e''x_e''$  and  $\omega_e'x_e'$  are anharmonicity parameters.

Fig. 2 presents the radial distributions of the dopant concentrations and absorption coefficients at fixed wavelengths in samples Nos 1–3. All the dopants, which are volatile elements or form volatile oxides, are absent in the middle of workpieces because of their diffusion from the glass to atmosphere during the collapse. Oxygen also diffuses into the glass during the collapse. The 203-nm absorption band with a maximum at a distance of 0.3 mm from the sample axis (Figs 2a, 2b), which provides the main contribution to the UV absorption in sample No. 2, is closest to the central dip. Because this absorption appears in an oxygen-enriched region, it can be attributed to oxidised sulphur (presumably, to  $\text{SO}$  molecules). Fig. 2b shows that, in this case, the sulphur weight concentration in the quartz glass reaches 0.5%. Such a high sulphur concentration in the glass obtained under conditions of oxygen deficiency suggests that the presence of oxygen prevents the sulphur penetration into the glass.

However, the formation of sulphur-related defects is determined not only by the interaction of the doped glass with oxygen. This process is also affected by chlorine whose



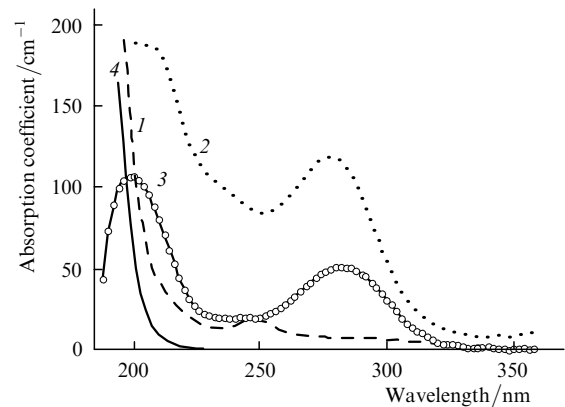
**Figure 2.** Radial distributions of the dopant concentrations and absorption coefficients at fixed wavelengths in samples Nos 1–3 of sulphur-doped quartz glasses. Vertical arrows indicate the regions of samples in which the absorption spectra were measured (see Fig. 3).

weight concentration in the middle of the workpiece may reach a few percent. Sample No. 3 (Fig. 2c) differs from No. 2 only by a higher chlorine content. Nevertheless, absorption measurements have shown (Fig. 1) that the sulphur bands at 203, 237, 280, 400, and 525 nm are absent in sample No. 3. We assume that chlorine may prevent the formation of the defects associated with sulphur. A distinguishing feature of sample No. 3 is the presence of anomalously strong absorption lines at 212 and 248 nm with absorption coefficients of 215 and 25  $\text{cm}^{-1}$ , respectively. In nondoped glasses, the absorption coefficient at  $\lambda = 248$  nm is no higher than 1–2  $\text{cm}^{-1}$ , and it is even lower for the 212-nm band. Stronger bands were observed in nitrogen-doped quartz glasses [8] with absorption coefficients at 248 and 212 nm of  $\sim 3$  and  $\sim 10$   $\text{cm}^{-1}$ , respectively.

By now, it has been established that the absorption band at 248 nm and the photoluminescence bands at 280 and 450 nm corresponding to it belong to silicon oxygen-deficient centres (ODCs). This colour centre is treated as either a defect of the  $\equiv \text{Si} - \text{Si} \equiv$  type (an oxygen vacancy [9, 10]), or a twofold coordinated neutral silicon atom =  $\text{Si}_0^0$

[11]. An intense luminescence line at 280 nm arising upon excitation into the 248-nm band additionally confirms that, in our case, this band is due to silicon ODCs. Although the 212-nm band is close to the band of the paramagnetic silicon  $E'$ -centre [12], it does not belong to it, because paramagnetic signals are not detected in this sample (they are below the sensitivity threshold of  $10^{14}$  spin.  $\text{cm}^{-3}$  for our EPR spectrometer). It was found in [8] that the intensity of the 212-nm band increases with the chlorine concentration. Therefore, in this study, we can only assume that silicon colour centres, which are somehow coupled to chlorine, are responsible for this band, and the oxygen deficiency in the glass network favours their formation.

Fig. 3 depicts the absorption spectra for samples Nos 2 and 3 in the regions shown in Fig. 2. One can see that at the periphery (at a distance exceeding 0.7 mm from the workpiece centre, Fig. 2b), the absorption bands due to sulphur colour centres and oxygen are absent [curve (1) in Fig. 3]. Only the band at 248 nm belonging to silicon ODCs is observed in the spectrum. Curve (2) measured at the absorption maxima at 203 and 280 nm in sample No. 2 shows the presence of the aforementioned sulphur centres. Curve (3) is interesting, because a well-resolved 203-nm band is observed in it due to the absence of a strong UV absorption wing. This proves the existence of the 203-nm band. A similar experiment performed with sample No. 3 [curve (4)] allows us to unambiguously conclude that this sample has no colour centres (presumably, SO interstitial molecules) responsible for the 203-nm band, and other sulphur absorption bands are also absent.

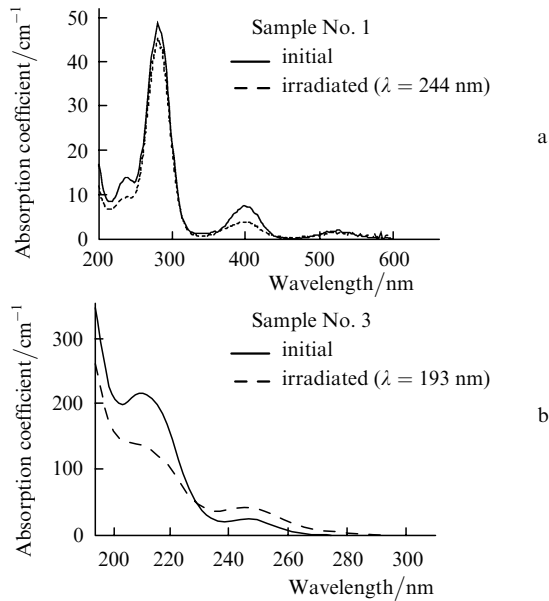


**Figure 3.** Absorption spectra of samples Nos 2 and 3 in the regions marked with vertical arrows in Fig. 2. Curve numbers correspond to the figures above these arrows.

### 3.2 Photosensitivity of colour centres

To estimate the prospect for using sulphur-doped glasses for creating photorefracting devices, we studied the photobleaching of their absorption bands for all of the three samples exposed to laser radiation. Fig. 4a shows the absorption spectra for sample No. 1 before and after irradiation by the second harmonic of an Ar laser at 244 nm. One can see from Fig. 4a that the intensity of the 280-nm band belonging to the  $\text{S}_2$  molecule remained virtually unchanged, indicating its low photosensitivity.

This is explained in [7] by the fact that sulphur molecules penetrate into glass pores mainly individually. Therefore, a reaction of molecular polymerisation into  $\text{S}_3 - \text{S}_8$  clusters is



**Figure 4.** Absorption spectra of sulphur-doped quartz-glass samples Nos 1 and 3 before and after laser irradiation at 244 and 193 nm. Measurements were performed in the regions with a maximum sulphur concentration.

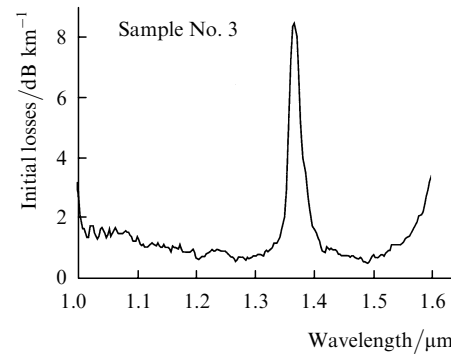
impossible. Moreover, it was shown in [6] that the photoexcitation of a sulphur molecule to high vibrational states of the  $B^3\Sigma_u^-$  term (i.e., into the short-wavelength wing of the 280-nm band) leads to its dissociation but without its observable photodissociation. It is most likely that sulphur atoms produced upon dissociation and being in the ground state  $^3P$  do not react with the glass network and, therefore, recombine into the initial  $S_2$  molecule. The intensities of the 237- and 400-nm bands decreased approximately by half. This means that the photosensitivity of  $S_2^+$  ions is high.

A high rate of thermal bleaching and photobleaching of these bands was reported in our study [13]. The ground energy state of the  $S_2^+$  ion is higher than that of the  $S_2$  molecule by 9.36 eV (the ionisation potential of the  $S_2$  molecule [14, p.150]), which is close to the glass energy gap. Therefore, an efficient decomposition of molecular ions can be expected during photo- and thermal excitation. This process occurs most likely through an electron capture by  $S_2^+$  ions from another centres or the glass network.

We also investigated the effect of 193-nm ArF-laser radiation on samples Nos 2 and 3. As was mentioned above, sample No. 2 has a stronger absorption band at 203 nm [Figs 2b and 3, curve (3)], which presumably belongs to SO molecules. We found that the intensity of this band did not change after the laser irradiation. Therefore, as the 280-nm band, this band is also not photosensitive. The behaviour of all the other bands is qualitatively similar to that of the corresponding bands of sample No. 1 irradiated at 244 nm. We observed the photocomposition of the 212-nm band (the absorption coefficient decreased by a factor of  $\sim 1.5$ ) in sample No. 3 after its irradiation by the ArF laser at 193 nm (Fig. 4b).

### 3.3 A sulphur-doped silica fibre and its photorefractive properties

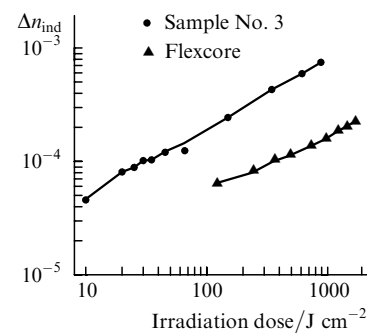
A fibre with a cut-off wavelength  $\lambda_{\text{cut}} = 0.95 \mu\text{m}$  and  $\Delta n = 0.006$  was drawn from a preform (sample No. 3) with



**Figure 5.** Spectrum of the initial optical losses in a single-mode fibre (sample No. 3) drawn from a sulphur-doped quartz-glass workpiece.

a sulphur and chlorine weight content in the core of 0.4 and 2 %, respectively. The optical loss spectrum for this fibre is shown in Fig. 5. The minimum loss at wavelengths of 1.31 and 1.55  $\mu\text{m}$  was  $0.4 \text{ dB km}^{-1}$ . Thus, the sulphur-doped glass is suitable for producing the core of low-loss fibres.

Fig. 6 presents a dose dependence of the induced refractive index for the 193-nm UV irradiation and, for comparison, a dose dependence of a germanosilicate Flexcore fibre with identical waveguide parameters. The fibre was manufactured by a conventional MCVD method and had the following parameters:  $\Delta n = 0.0065$ ,  $\lambda_{\text{cut}} = 0.96 \mu\text{m}$ , and the  $\text{GeO}_2$  molecular content in the core was 4.5 %. One can see from Fig. 6 that the sulphur-doped fibre is significantly more sensitive to UV irradiation than the germanosilicate fibre. The highest value of the induced refractive index measured in the sulphur-doped fibre was  $7.8 \times 10^{-4}$ . Moreover, the character of the dose dependence suggests that this value is not the maximum attainable for this sample.



**Figure 6.** Refractive index induced by ArF-laser radiation at 193 nm versus the irradiation dose for a sulphur-doped silica fibre (sample No. 3) and a germanosilicate Flexcore fibre.

Studies of the photosensitivity of the fibre irradiated at a wavelength of 244 nm have shown the absence of the induced refractive index ( $\Delta n_{\text{ind}} < 0.5 \times 10^{-4}$ ) at doses of  $50 \text{ kJ cm}^{-2}$  and a power density of  $50 \text{ W cm}^{-2}$ . Note that, under the given irradiation conditions,  $\Delta n_{\text{ind}}$  in the germanosilicate fibre reaches  $\sim 3 \times 10^{-4}$ , and the 244-nm radiation falls within the absorption band of germanium ODCs. For the sulphur-doped fibre, this band belongs to silicon ODCs, and the absence of photosensitivity upon irradiation with light within the 244-nm band testifies to different efficiencies

of the decay of the absorption bands of silicon and germanium ODCs exposed to laser irradiation.

To date, several mechanisms have been proposed to explain the nature of the photorefractive effect in bulk samples and silica fibres exposed to UV radiation. One of the first and most general approaches is based on the fundamental link between the refractive index and absorption coefficient through the Kramers–Kronig dispersion relations [15]. The main difficulty associated with the use of this approach is due to an insufficient width of the spectral range within which the absorption spectra are measured. Therefore, the theoretical values of the induced refractive index are usually underestimated compared to the experimentally observed values. An approximate formula presented in [16] for evaluating the contribution of the change in the UV absorption to the induced refractive index measured at 1.5  $\mu\text{m}$  has the form

$$\Delta n_{\text{ind}} = \left( \frac{\lambda}{2\pi^2} \right) \left( \frac{W}{\hbar\omega} \right) \Delta\alpha_{\text{max}},$$

where  $\Delta\alpha_{\text{max}}$  is the maximum value of the induced absorption at the frequency  $\omega$  and  $W$  is the half-width at half maximum of the induced-absorption spectrum.

Fig. 4 shows that the maximum  $\Delta\alpha_{\text{max}}$  ( $\sim 130 \text{ cm}^{-1}$ ) resulting from the ArF-laser irradiation is observed for the band at 212 nm with the width  $W = 0.7 \text{ eV}$ . Substituting these data into the above formula, we obtain  $\Delta n_{\text{ind}} = 1.5 \times 10^{-5}$ . However, the experimental  $\Delta n_{\text{ind}}$  value is higher by more than an order of magnitude. Such a discrepancy indicates that the main region of changes in the absorption spectra actually lies beyond the observation range (190–600 nm).

The potentially attainable  $\Delta n_{\text{ind}}$  value in a fibre doped with sulphur and chlorine can be  $> 10^{-3}$ . This fact combined with a rather low concentration of dopants and a low optical loss evokes a great interest in such fibres from the viewpoints of both their practical application and further investigation of their properties. As to the light-induced changes in the refractive index, it is especially important to understand the nature of the absorption band at 203 nm.

#### 4. Conclusions

We studied samples of sulphur-doped quartz glasses produced by the SPCVD method under various synthesising conditions and investigated their spectral characteristics in the UV and visible regions. The absorption band at 280 nm with a vibrational structure was assigned to interstitial  $\text{S}_2$  molecules, and the bands at 237 and 400 nm were assigned to the interstitial  $\text{S}_2^+$  ion ( $\text{S}_2$  and  $\text{S}_2^+$  are weakly bound to the glass network). It was shown that a high concentration of chlorine prevents the formation of interstitial  $\text{S}_2$  molecules and  $\text{S}_2^+$  ions in a sulphur-doped quartz glass.

We showed that such a glass is suitable for producing optical fibres with low losses within the main telecommunication windows at 1.3 and 1.55  $\mu\text{m}$ . A Bragg grating was written in a fibre with such properties. The induced refractive index in this grating is comparable to that in analogous refractive-index gratings in germanosilicate fibres.

**Acknowledgements.** The authors thank H.G. Limberger (Institute of Applied Physics, Lausanne, Switzerland) for his assistance in experiments on recording Bragg gratings. This work was supported by the Russian Foundation for Basic Research (Grant Nos 00-02-17400 and 00-15-96679).

#### References

1. Askins C.G., in *Defects SiO<sub>2</sub> and Related Dielectrics* (Amsterdam: Kluwer Acad. Publ., 2000) V.2, p.391.
2. Dianov E.M., Golant K.M., Mashinsky V.M., Medvedkov O.I., Nikolin I.V., Sazhin O.D., Vasilev S.A. *Electron. Lett.*, **33**, 1334 (1997).
3. Bilodeau F., Malo B., Albert J., Johnson D.C., Hill K.O., Hibino Y., Abe M., Kawachi M. *Opt. Lett.*, **18**, 953 (1993).
4. Larionov Yu.V., Rybaltovskii A.A., Semenov S.L., Bubnov M.M., Dianov E.M. *Kvantovaya Elektron.*, **32**, 124 (2002) [*Quantum Electron.*, **32**, 124 (2002)].
5. Dianov E.M., Golant K.M., Karpov V.B., Khrapko R.R., Kurkov A.S., Mashinsky V.M., Protopopov V.N. *Proc. SPIE Int. Soc. Opt. Eng.*, **2425**, 53 (1994).
6. Zavorotnyi Yu.S., Lutsko E.V., Rybaltovskii A.O., Chernov P.V., Sokolov V.O., Khrapko R.R. *Phys. Khim. Stekla*, **27**, 495 (2001).
7. Gerasimova V.I., Zavorotnyi Yu.S., Rybaltovskii A.O., Chernov P.V., Sazhin O.D., Khrapko R.R., Frolov A.A. *Phys. Khim. Stekla*, **28**, 8 (2002).
8. Golant K.M., Dianov E.M., Khrapko R.R., Tomashuk A.L. *Proc. SPIE Int. Soc. Opt. Eng.*, **4083**, 2 (2000).
9. Amosov A.V. *Phys. Khim. Stekla*, **9**, 569 (1983).
10. Sulimov V.B., Sokolov V.O. *J. Non-Cryst. Solids*, **191**, 260 (1995).
11. Skuja L.N., Streletsky A.N., Pakovich A.B. *Solid State Commun.*, **50**, 1069 (1984).
12. Skuja L.N. *J. Non-Cryst. Solids*, **239**, 16 (1998).
13. Gerasimova V.I., Rybaltovskii A.O., Chernov P.V., Zimmerer G. *Phys. Khim. Stekla*, **28**, 89 (2002).
14. Huber K.P., Herzberg G. *Constants of Diatomic Molecules* (New York: Reinhold, 1979).
15. Hand D.P., Russell P.St.J. *Opt. Lett.*, **15**, 102 (1990).
16. Sokolov V.O., Sulimov V.B. *Volok. Opt. Mater. Ustr.* (3), 35 (2000).