

Optical properties of fibres with aluminophosphosilicate glass cores

M.M. Bubnov, A.N. Guryanov, K.V. Zotov, L.D. Iskhakova, S.V. Lavrishchev, D.S. Lipatov, M.E. Likhachev, A.A. Rybaltovsky, V.F. Khopin, M.V. Yashkov, E.M. Dianov

Abstract. The optical properties of fibres with aluminophosphosilicate (APS) glass cores have been studied at Al_2O_3 and P_2O_5 concentrations varied independently from 0 to 20%, and the ranges of dopant concentrations that ensure an optical loss level acceptable for the fabrication of active fibres have been established. The origin of the increased losses observed previously in APS fibres containing excess phosphorus pentoxide has been identified, and the contamination source responsible for such losses in our fibres has been eliminated.

Keywords: aluminophosphosilicate optical fibres, optical losses, large mode field diameter fibres.

1. Introduction

The significant recent advances in raising the output power of fibre lasers (to above 1 kW in continuous mode and to above 1 MW of peak power in pulsed operation) have made them a highly attractive alternative to conventional solid-state lasers [1, 2]. The performance of fibre lasers is limited to a significant degree by nonlinear processes that take place in the active fibre at high power levels. The threshold for such processes can be raised by reducing the active-fibre length or increasing the fundamental mode field diameter, which enables a reduction in the optical power density in the fibre core.

To reduce the active-fibre length with no changes in pump power absorption efficiency or optical gain, one must raise the rare-earth content of the fibre core. The solubility of rare-earth oxides in silica glass is well known to be rather low. In view of this, the active-fibre core is typically doped with aluminium oxide or phosphorus pentoxide, which raise the rare-earth solubility. To limit the optical loss to an acceptable level, the glass should contain at least 10 aluminium or phosphorus atoms per rare-earth atom [3]. The fundamental mode field size (core diameter) can be in-

creased, while maintaining single-mode operation of the fibre, only if an appropriate reduction in the refractive index of the fibre core is ensured by decreasing the percentage of Al_2O_3 or P_2O_5 (index-raising dopants) in the core [4, 5]. Thus, the above ways of raising the threshold for nonlinear effects are mutually exclusive.

One possible solution to this problem is to dope the core glass with an effective index-lowering agent, e.g., with fluorine. Note, however, that such doping markedly reduces the melting point of the core glass, leading to active vapourisation of the oxide dopants and bubble generation during the porous layer melting and preform collapse steps. For this reason, phosphosilicate and aluminosilicate glasses can be readily doped with fluorine to only 1 wt %, which reduces their refractive index by just 0.003. To further raise the fluorine concentration, the preform fabrication process must be significantly modified.

An alternative approach is to use Al_2O_3 – P_2O_5 – SiO_2 glasses. As shown by Lemaire et al. [6], codoping of silica glass with roughly equimolar amounts of Al_2O_3 and P_2O_5 ($\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5 \cong 1$) reduces its refractive index. The effect persists up to an $\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5$ content of 30 mol %, which makes such glasses potentially attractive as doping hosts for the fabrication of active fibres with a high rare-earth concentration in the core and a large fundamental mode field diameter.

The efficiency of fibre lasers is highly dependent on optical losses in the active fibre. Optical losses in fibres codoped with P_2O_5 and Al_2O_3 are essentially unexplored. It is known only that Al_2O_3 doping to above 4 mol % sharply increases the optical loss in silica fibres because of crystallisation [7]. Doping with a small amount of P_2O_5 (1 %–2 %) was shown to suppress the crystallisation of aluminosilicate glasses and to reduce losses to below 1 dB km⁻¹ [8]. In addition, Vienne et al. [9] reported an increase in 1200-nm optical losses from 100 to 500 dB km⁻¹ as the Al_2O_3 content of active silica fibres containing 11 %–13 % P_2O_5 was raised from 0 to 8 mol %. Unfortunately, they did not report optical loss spectra of their fibres, nor did they discuss the origin of the loss. In this paper, we report optical loss measurements in fibres with Al_2O_3 – P_2O_5 – SiO_2 glass cores in a wide spectral range (200–1700 nm) at Al_2O_3 and P_2O_5 contents varied independently in the range 0–20%.

2. Preform fabrication

Fibre preforms were produced by modified chemical vapour deposition (MCVD) [10]. Typical precursors in this process are low-boiling liquids, such as SiCl_4 , GeCl_4 , BBr_3 , POCl_3

M.M. Bubnov, K.V. Zotov, L.D. Iskhakova, S.V. Lavrishchev, M.E. Likhachev, A.A. Rybaltovsky, E.M. Dianov Fiber Optics Research Center, Russian Academy of Sciences, ul. Vavilova 38, 119333 Moscow, Russia; e-mail: likhachev@fo.gpi.ru;
A.N. Guryanov, D.S. Lipatov, V.F. Khopin, M.V. Yashkov Institute of Chemistry of High-Purity Substances, Russian Academy of Sciences, ul. Tropinina 49, 603950 Nizhnii Novgorod, Russia

Received 18 November 2008; revision received 16 June 2009

Kvantovaya Elektronika 39 (9) 857–862 (2009)

Translated by O.M. Tsarev

and $C_2F_3Cl_3$. Since there are no volatile liquid precursors to aluminium, Al_2O_3 doping is commonly performed via impregnation of a porous glass layer with an aluminium salt solution, followed by drying, oxidation and vitrification [11, 12]. Clearly, in this doping procedure the colouring impurities present in the aluminium precursor and responsible for increased optical losses pass into the glass.

In this work, silica glass was doped with all components by a vapour phase process. The aluminium precursor was $AlCl_3$ (99.999% purity on metals basis). As distinct from the other precursors, $AlCl_3$ is a low-volatile solid under ordinary conditions. To achieve an acceptable vapour pressure of this compound, it must be heated to 125–140°C. Moreover, under ordinary conditions $AlCl_3$ reacts with $POCl_3$ to form complexes [13]. In view of this, our MCVD apparatus was supplemented with a system for evaporation of solid precursors and vapour delivery. $AlCl_3$ powder was placed in a container thermostated at 130°C. The $AlCl_3$ vapour was delivered by argon carrier gas to the reaction zone through a separate heated line and was mixed with the other components inside the substrate tube. In all other respects, the procedure we used to produce preforms with aluminophosphosilicate (APS) glass cores was identical to the standard MCVD process. Note that, in contrast to the solution doping technique, vapour phase doping ensures high Al_2O_3 concentration in silica glass and enables control over the Al_2O_3 profile both along and across the preform. Moreover, we expect this process to be capable of removing the most strongly absorbing colouring impurities from Al_2O_3 vapour because many of them have boiling points well above 130°C: $FeCl_3$, 320°C; $FeCl_2$, 1026°C; $CuCl$, 1690°C [13].

3. Optical characterisation of the fibres

The elemental composition of the preforms was determined by X-ray microanalysis (JEOL JSM-5910LV). Refractive index profiles were obtained with a York Technology P102 preform analyser. The preforms were drawn into multi-

mode fibres 125 μm in outer diameter and 30 μm in core diameter. Optical losses in the fibres were measured by the standard cut-back technique.

Doping with phosphorus pentoxide or alumina increases the refractive index of silica glass roughly in proportion to the molar concentration of the dopant. In the range 0–17 mol% P_2O_5 , the increase in the refractive index of silica glass is given by [4]

$$\Delta n = 0.88 \times 10^{-3} C_{P_2O_5}, \quad (1)$$

where $C_{P_2O_5}$ is the mole percent of P_2O_5 . Alumina doping leads to a substantially larger increase in the refractive index of silica glass. According to our measurements,

$$\Delta n = 2.5 \times 10^{-3} C_{Al_2O_3}, \quad (2)$$

where $C_{Al_2O_3}$ is the mole percent of Al_2O_3 .

Relation (2) agrees with earlier data [5] within experimental uncertainties:

$$\Delta n = 2.3 \times 10^{-3} C_{Al_2O_3}. \quad (3)$$

Figure 1a illustrates the effect of doping with P_2O_5 (15%) and Al_2O_3 (14%) on the refractive index of the preforms. Codoping with roughly equimolar amounts of phosphorus pentoxide and alumina reduces the refractive index of the preforms to below the level of undoped silica glass.

This effect was first explained by Kosinski et al. [14], who showed using Raman spectroscopy and nuclear magnetic resonance that the network of silica glass codoped with Al_2O_3 and P_2O_5 contained $AlPO_4$ structural units in the form of $\equiv P-O-Al\equiv$, each substituting for two silicon atoms linked by an oxygen ($\equiv Si-O-Si\equiv$). This substitution is facilitated by the fact that the sum of the ionic radii of Al^{3+} and P^{5+} is close to twice the ionic radius of Si^{4+} , so that Al^{3+} and P^{5+} ions take up fourfold coordination in silica glass. Thermodynamic modelling of APS glass formation suggests that almost all the Al_2O_3 and P_2O_5 molecules

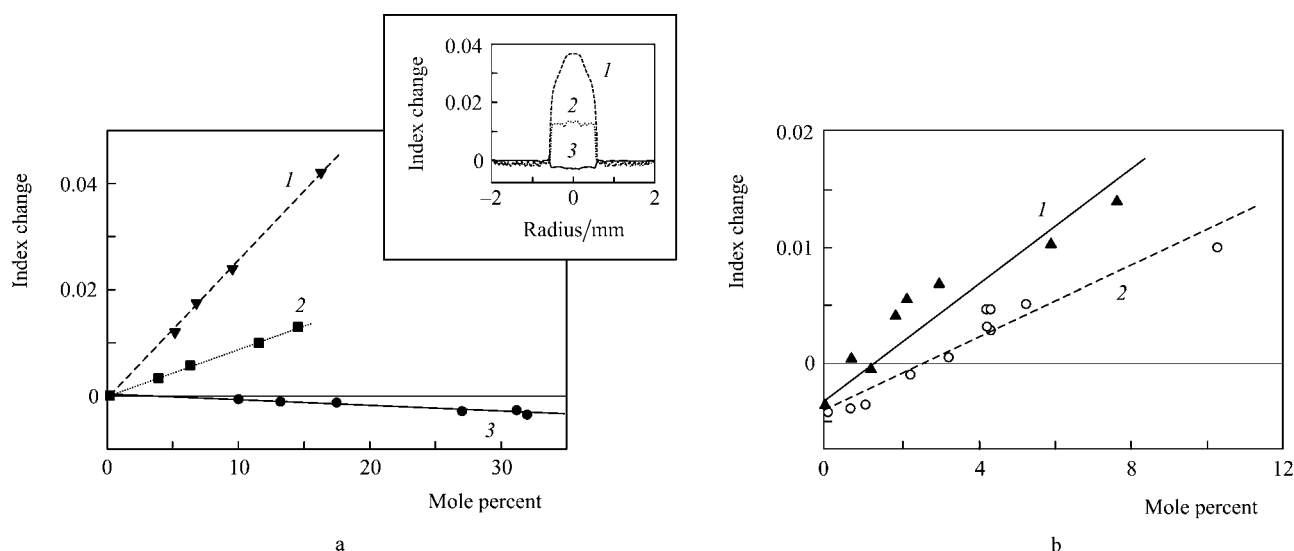


Figure 1. (a) Effect of (1) Al_2O_3 , (2) P_2O_5 and (3) $AlPO_4$ concentrations on the refractive index of silica glass. Inset: refractive index profiles in preforms doped with (1) 14% Al_2O_3 , (2) 15% P_2O_5 and (3) 15% Al_2O_3 + 17% P_2O_5 . (b) Effect of excess (1) Al_2O_3 and (2) P_2O_5 on the refractive index of silica glass containing 25% $AlPO_4$.

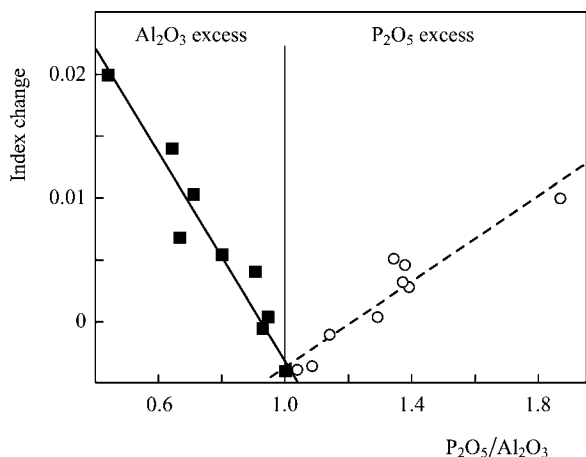


Figure 2. Effect of the P_2O_5/Al_2O_3 molar ratio on the refractive index of silica glass.

combine to form $AlPO_4$ structural groups in both the melt and glass [15]. The stability of these groups is evidenced by the high melting point (over $1600^\circ C$) of crystalline $AlPO_4$ [16].

Our experimental data on the refractive index of silica glass doped with equimolar amounts of Al_2O_3 and P_2O_5 can be represented in terms of $AlPO_4$ concentration (Fig. 1a):

$$\Delta n = -0.96 \times 10^{-4} C_{AlPO_4}, \quad (4)$$

This relation agrees with earlier data [15].

When one of the oxide dopants is added in excess of the equimolar ratio, all the other dopant is incorporated in $AlPO_4$ groups, whereas the excess dopant is present in the silica glass in its usual form. Independent of the $AlPO_4$ concentration, the molar refractivity of excess alumina, $\Delta C_{Al_2O_3}$, is roughly the same as in aluminosilicate glass (Fig. 1b):

$$\Delta n = 2.4 \times 10^{-3} C_{Al_2O_3}. \quad (5)$$

In contrast, the molar refractivity of excess phosphorus pentoxide, $\Delta C_{P_2O_5}$, is substantially higher than that in phosphosilicate glass (Fig. 1b):

$$\Delta n = 1.4 \times 10^{-3} C_{P_2O_5}. \quad (6)$$

Figure 2 illustrates the effect of the P_2O_5/Al_2O_3 ratio on the refractive index of the codoped silica glass. The sharp break in the plot indicates that, at a roughly equimolar P_2O_5/Al_2O_3 ratio, the dopants are present predominantly as $AlPO_4$ groups.

To study optical losses in silica glass codoped with Al_2O_3 and P_2O_5 , we fabricated APS fibres containing an excess of phosphorus pentoxide or alumina. The refractive index of their core exceeded that of silica glass by $(1-15) \times 10^{-3}$. To reduce the leakage and bending losses in the fibres with $\Delta n = (1-3) \times 10^{-3}$, a fluorine-doped reflective cladding was produced, which had a refractive index lower than that of silica glass by 0.003.

Based on the loss measurement results, the fibres can be divided into three distinct groups (Fig. 3).

Group I comprises the fibres with cores containing an excess of Al_2O_3 and less than 15 mol % P_2O_5 . These fibres have a relatively low optical loss level, within 30 dB km^{-1} in the spectral range 800–1700 nm [Fig. 4, spectrum (1)]. Group

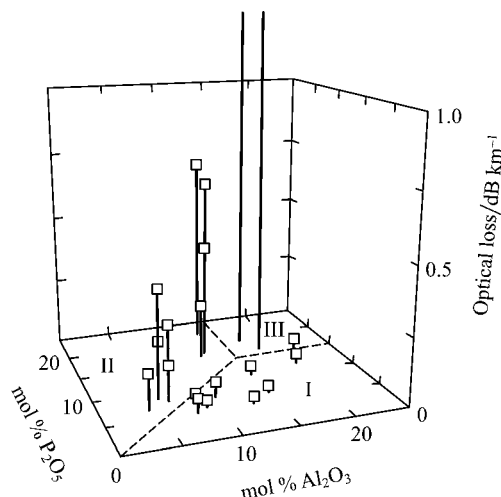


Figure 3. 1200-nm optical loss as a function of Al_2O_3 and P_2O_5 contents in the APS fibre core; the dashed lines indicate the boundaries between groups I–III.

II comprises the fibres with cores containing an excess of P_2O_5 and no more than 15 mol % Al_2O_3 [Fig. 4, spectrum (2)]. Their IR spectra show a very broad absorption band centred at 1200 nm, with an intensity of $100-600 \text{ dB km}^{-1}$.

If both the Al_2O_3 and P_2O_5 contents exceeded $\sim 15 \text{ mol \%}$ (group III), the preforms had white, opaque cores. The fibres drawn out from those preforms showed much higher losses, $10-30 \text{ dB m}^{-1}$. The weak wavelength dependence of the optical loss in group III [Fig. 4, spectrum (3)] suggests that the loss might be due to the scattering by large-scale inhomogeneities, presumably associated with phase separation or crystallisation of the glass. Structural studies [17] indicate that, up to an $AlPO_4$ content of at least 20 %, the $AlPO_4$ groups in silica glass form a solid solution with the host material, that is, the glass retains $Al-O-P$ structural components. At considerably higher $AlPO_4$ concentrations, the glass contains, in addition, $Si-O-P$ and $Si-O-Al$ structural units [17]. Note that the range of Al_2O_3 and P_2O_5 concentrations in which high background losses occur in APS fibres may vary. In particular, when the contents of both oxides are below 15 mol %, the background loss may

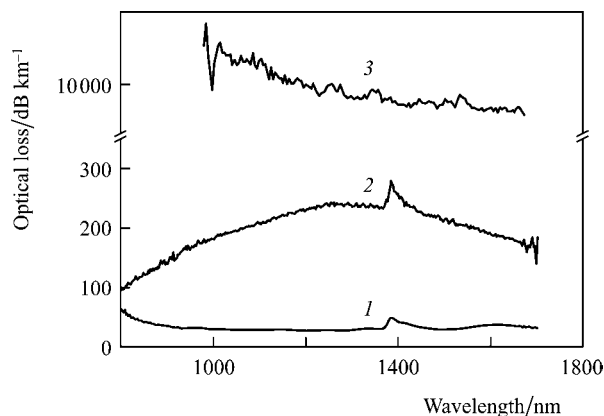


Figure 4. Typical optical loss spectra of (1) aluminium-enriched (8.4 mol % Al_2O_3 + 7.2 mol % P_2O_5), (2) phosphorus-enriched (7 mol % Al_2O_3 + 10 mol % P_2O_5) and (3) heavily doped (16 mol % Al_2O_3 + 18 mol % P_2O_5) APS fibres.

reach 100 dB km^{-1} and above, but it can be suppressed by adjusting fibre drawing conditions. It seems likely that crystallisation centres may form as well at AlPO_4 contents below 30%, but rapid cooling of the glass in the fibre drawing step impedes this process.

From the practical point of view, the issue of most interest is to understand the origin of optical losses in the group II fibres (Fig. 3). Increased optical losses in APS-core fibres were also reported previously. As mentioned above, Vienne et al. [9] observed an increase in 1200-nm optical losses from 100 to 500 dB km^{-1} as the Al_2O_3 content of silica fibres containing 11%–13% P_2O_5 was raised from 1% to 8%. Very recently, when this study was in progress, Unger et al. [18] also reported the optical properties of fibres with Al_2O_3 – P_2O_5 – SiO_2 cores, but in a narrower range of doping levels. In that study, preforms were doped via porous layer impregnation with an aluminium salt solution, followed by oxidation and vitrification, in contrast to the vapour phase process used here to dope silica glass with Al_2O_3 . Unger et al. [18] reported the fibres containing 8% P_2O_5 to have a broad absorption band in the range 700–1700 nm, centred at 1200 nm, whose intensity increased from 150 to 600 dB km^{-1} as the mole fraction of Al_2O_3 was raised from 0.4% to 3.3%. At the same time, they detected no additional optical losses when the APS core contained an excess of Al_2O_3 .

To clarify the origin of the absorption band in P_2O_5 -enriched APS fibres, optical losses in fibres differing in core glass composition were measured in a wide spectral range, from 200 to 1700 nm (Fig. 5). In fibre (1), singly doped with phosphorus pentoxide (12% P_2O_5), and fibre (2), singly doped with alumina (4% Al_2O_3), the 1200-nm optical losses were 1 and 12 dB km^{-1} , respectively, attesting to high purity of the starting reagents. In the spectra of those fibres, the characteristic absorption band around 1200 nm was missing. The absorption around 250 nm in fibre (1) seems to be due to singlet–singlet excitation of the $\text{O}=\text{P}-\text{O}-\text{P}=\text{O}$ centre [19]. This feature is also present in the spectrum of fibre (3), containing an excess of P_2O_5 . The spectra of fibre (2), singly doped with alumina, and fibre (4), containing an excess of Al_2O_3 , show the well-known absorption band at 550 nm, due to the aluminium–oxygen hole centre ($\text{Al}-\text{OHC}$) [20]. Thus, the present results suggest that APS fibres containing

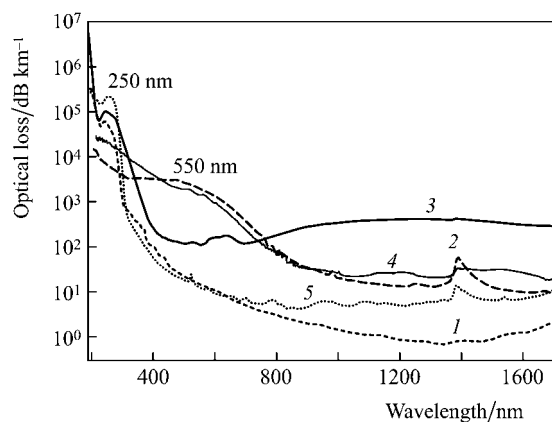


Figure 5. Optical loss spectra of (1) phosphosilicate fibre (12% P_2O_5), (2) aluminosilicate fibre (4% Al_2O_3), (3) phosphorus-enriched APS fibre (11% Al_2O_3 + 14.8% P_2O_5), (4) aluminium-enriched APS fibre (11% Al_2O_3 + 8% P_2O_5) and (5) phosphorus-enriched APS fibre after replacement of the rotary joint (4% Al_2O_3 + 8% P_2O_5).

an excess of P_2O_5 or Al_2O_3 are similar in glass network structure to phosphosilicate or aluminosilicate glass, respectively. This observation leads us to assume that the absorption band at 1200 nm is due not to the presence of colour centres in the APS glass but to other factors.

In silica glass, Fe can be present in the form of Fe^{3+} and Fe^{2+} . The Fe^{3+} ion leads to strong absorption at wavelengths under 400 nm [21]. Fe^{2+} in silica glass is characterised by a broad absorption band around 1200 nm, very similar to the one we observe in APS fibres containing an excess of P_2O_5 . Note that Fe^{2+} has a very large extinction coefficient, $\sim 10^7 \text{ dB km}^{-1} \%$ at 1200 nm [21, 22].

In the MCVD process, chloride precursors are oxidised at very high temperatures (1200–1600 °C) in the presence of excess oxygen, and the process is accompanied by chlorine release. One might expect that, under such conditions, Fe atoms entering the reaction zone oxidise to Fe_2O_3 , so that the absorption band at 1200 nm, due to Fe^{2+} , must be missing. Thermodynamic modelling results suggest however that, at high MCVD temperatures, both Fe(II) and Fe(III) chlorides may be formed, the percentage of Fe^{2+} being larger at higher process temperatures. Subsequently, the valence of the Fe ions depends significantly on the glass composition. In particular, in alkali borosilicate glasses the percentage of Fe^{2+} increases with Na_2O and SiO_2 concentration [23]. In one of the first reports dealing with the fabrication of phosphosilicate-core fibres, Gambling et al. [24] pointed out that Fe impurities were particularly undesirable in such fibres because they had a valence of $2+$. Moreover, they found that, in contrast to the other precursors used in the MCVD process (SiCl_4 , GeCl_4 , BCl_3 , SF_4 , CF_4), phosphorus oxychloride, POCl_3 , corroded the stainless steel valve in their gas distribution system. As a result, the phosphosilicate-core fibres showed a sharp increase in absorption at wavelengths above 700 nm, characteristic of the Fe^{2+} ion.

In our MCVD apparatus, all the parts of the chloride delivery system were made of glass or Teflon. The only stainless steel part was the bearing sleeve of the rotary joint connecting the chloride delivery system and the rotating substrate tube, but it was not exposed to any chlorides. The low optical loss level ($\sim 1 \text{ dB km}^{-1}$ in the wavelength range 1000–1500 nm) in our phosphosilicate-core fibres indicates that the deposited glass was not contaminated with Fe ions. At the same time, after unsealing the rotary joint, the inner surface of the sleeve was found to be corroded (Fe_2O_3 traces), indicating that this part had been exposed to POCl_3 vapour. Note that, when the glass was codoped with Al_2O_3 and P_2O_5 , the rotary joint was heated to $\sim 200^\circ\text{C}$ in order to preclude AlCl_3 vapour condensation. It seems likely that the Teflon insulation of the sleeve was damaged, which led to contamination of the glass with Fe ions.

The APS glass containing an excess of P_2O_5 is similar in properties to the phosphosilicate glass and, accordingly, has an absorption band centred at 1200 nm, characteristic of the Fe^{2+} ion. In the optical loss spectra of the aluminosilicate-core fibres and APS fibres containing an excess of Al_2O_3 , the 1200-nm band is missing. It may be assumed that, in the aluminosilicate glass and the APS glass containing an excess of Al_2O_3 , where the phosphorus pentoxide is incorporated in AlPO_4 groups and which, accordingly, is similar in properties to the aluminosilicate glass, the valence of the Fe is $3+$. Note that the aluminosilicate fibres were most likely not contaminated with iron oxides because no POCl_3 was fed to the system in that case. This assumption is

supported by the fact that, at wavelengths below 400 nm, the optical losses in the APS fibres containing an excess of Al_2O_3 are higher than those in the aluminosilicate-core fibres, which can be accounted for by the contribution of Fe^{3+} .

When the bearing sleeve was replaced by one from niobium, the 1200-nm absorption in the APS fibres containing an excess of Al_2O_3 dropped from 100–500 to 5–15 dB km^{-1} (Fig. 6). The absorption spectrum measured in a wide wavelength range after replacement of the sleeve [Fig. 5, spectrum (5)] differed little from that of the phosphosilicate-core fibre before the replacement [Fig. 5, spectrum (1)]. To further ascertain the origin of the absorption band centred at 1200 nm, iron impurities were added to the core glass in a preform. In the fibre drawn out from that preform, the 1200-nm absorption was a hundred times stronger (40 dB m^{-1}) in comparison with the other fibres studied. Even in that case, however, the concentration of iron was too low to directly detect it. In particular, neither in that sample (which was known to contain iron) nor in the other samples studied was iron detected with certainty by electron paramagnetic resonance or ICP mass spectrometry. Thus, our results strongly suggest that the absorption band centred around 1200 nm is not intrinsic to the APS fibres containing excess P_2O_5 but is due to unintentional Fe^{2+} impurities.

This hypothesis sheds light on the origin of the optical losses observed in APS fibres by Unger et al. [18]. They used the solution doping technique, which is inherently more susceptible to contamination effects in comparison with vapour phase doping. In particular, iron oxide contamination may originate from the preparation of the aluminium salt solution and solution impregnation of the porous layer. It should also be emphasised that the purity of commercially available aluminium salts is no better than 99.999% on metals basis. As a rule, iron compounds account for about 10% of the total amount of metallic impurities, and their weight fraction in aluminium salts may exceed 1 ppm. Therefore, the 1200-nm absorption in silica glass doped with alumina to a mole fraction of several percent may reach 10–100 dB km^{-1} if all the iron ions have a valence of $2+$. If the iron content exceeds 10% of the total amount of metallic impurities or the aluminium salt is insufficiently pure, the

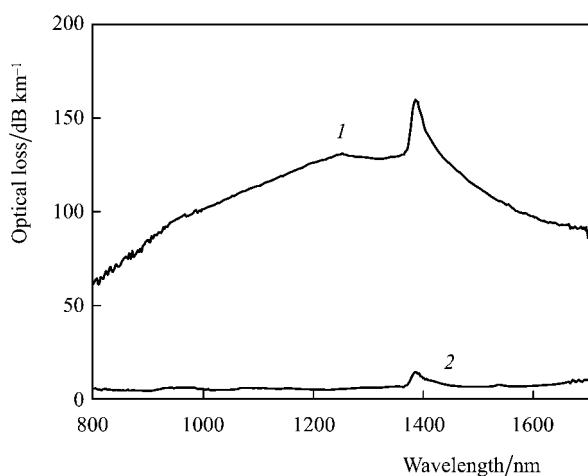


Figure 6. Optical loss spectra of APS fibres with an excess of P_2O_5 (4% Al_2O_3 + 8% P_2O_5) (1) before modification to the MCVD system and (2) after replacement of the bearing sleeve with one from niobium.

1200-nm loss may reach 100–600 dB km^{-1} , as was observed by Unger et al. [18]. In the P_2O_5 -free fibres, as well as in the APS fibres containing an excess of Al_2O_3 , the iron incorporated in the core is in the valence state $3+$, and there is no absorption at 1200 nm [18]. The glass doped with 0.4%–3.3% alumina and 8% P_2O_5 contains Fe^{2+} ions, and the 1200-nm absorption increases with Al_2O_3 content.

4. Conclusions

The present results on the optical properties of fibres with various alumina and phosphorus pentoxide concentrations in the core are the first to demonstrate that the optical losses in APS fibres containing an excess of phosphorus can be reduced to a level of $\sim 5 \text{ dB km}^{-1}$. When the mole fraction of Al_2O_3 or P_2O_5 is below 15%, the optical losses in the fibres can be reduced to a sufficiently low level ($\sim 10 \text{ dB km}^{-1}$), which enables such APS hosts to be used for the fabrication of active fibres. Experimental evidence is presented that the increased losses observed previously in APS fibres containing excess phosphorus pentoxide arise from contamination of the preforms with Fe ions. The optical loss spectra of our fibres in the range 200–1700 nm indicate that the APS fibres containing excess P_2O_5 are similar in optical properties (position and intensity of absorption bands) to binary phosphosilicate glasses, while the APS fibres with an excess of Al_2O_3 are similar to aluminosilicate fibres.

References

- Jeong Y., Sahu J.K., Payne D.N., Nilsson J. *Opt. Express*, **12**, 6088 (2004).
- Röser F., Eidam T., Rothhardt J., Schmidt O., Schimpf D.N., Limpert J., Tunnermann A. *Opt. Lett.*, **32**, 3495 (2007).
- Arai K., Namikawa H., Kumata K., Honda T., Ishii Y., Handa T. *J. Appl. Phys.*, **59**, 3430 (1986).
- Bubnov M.M., Dianov E.M., Egorova O.N., Semjonov S.L., Guryanov A.N., Khopin V.F., DeLiso E.M. *Proc. SPIE Int. Soc. Opt. Eng.*, **4083**, 12 (2000).
- Aramaki S., Roy R. *J. Am. Ceram. Soc.*, **45**, 229 (1962).
- Lemaire P.J., MacChesney J.B., Simpson J.R. US Patent No. 4.830.463 (1989).
- Ohmory Y., Honawa F., Nakahara M. *Electron. Lett.*, **18**, 761 (1982).
- Scott C.J. *Techn. Dig. Top. Meet. OFC Conf.* (New Orleans: OSA, 1984) p. 70.
- Vienne G.G., Brocklesby W.S., Brown R.S., Chen Z.J., Minelly J.D., Roman J.E., Payne D.N. *Opt. Fiber Technol.*, **2**, 387 (1996).
- Nagel S.R., MacChesney J.B., Walker K.L. *IEEE J. Quantum Electron.*, **18**, 459 (1982).
- Townsend J.E., Poole S.B., Payne D.N. *Electron. Lett.*, **23**, 329 (1987).
- Khopin V.F., Umnikov A.A., Gur'yanov A.N., Bubnov M.M., Senatorov A.K., Dianov E.M. *Neorg. Mater.*, **41**, 363 (2005).
- Furman A.A. *Neorganicheskie khloridy* (Inorganic Chlorides) (Moscow: Khimiya, 1980) p. 147.
- Kosinski S.G., Krol D.M., Duncan T.M., Douglass D.C., MacChesney J.B., Simpson J.R. *J. Non-Cryst. Sol.*, **105**, 45 (1988).
- DiGiovanni D.J., MacChesney J.B., Kometani T.Y. *J. Non-Cryst. Solids*, **113**, 58 (1989).

16. Rokita M., Handke M., Mozgawa W. *J. Mol. Struct.*, **450**, 213 (1998).
17. Handke M., Rokita M., Mozgawa W. *Vib. Spectrosc.*, **19**, 419 (1999).
18. Unger S., Schwuchow A., Dellith J., Kirchof J. *Proc. SPIE Int. Soc. Opt. Eng.*, **6469**, 646913 (2007).
19. Dianov E.M., Koltashev V.V., Plotnichenko V.G., Sokolov V.O., Sulimov V.B. *Fiz. Khim. Stekla*, **24**, 693 (1998).
20. Hosono H., Kawazoe H. *Nucl. Instrum. Methods Phys. Res.*, **B91**, 395 (1994).
21. Schultz P.C. *J. Am. Ceram. Soc.*, **57**, 309 (1974).
22. Olshansky R. *Rev. Mod. Phys.*, **51**, 341 (1979).
23. Newns G.R. *Proc. 2nd Europ. Conf. on Opt. Commun.* (Paris, 27–30 Sept., 1976) p. 21.
24. Gambling W.A., Payne D.N., Hammond C.R., Norman S.R. *IEEE Proc.*, **123**, 570 (1976).