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# Refractive Index of Aluminophosphosilicate Glass in Optical Fibers near $AlPO_4$ Join

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**Abstract:** The minimum refractive index of the aluminophosphosilicate (APS) core in optical fibers has been determined for a wide range of phosphorous and aluminum concentrations. It was found that the APS core refractive index became higher by ~0.0005–0.0012 as compared to that in optical fiber preform. The analysis of the measured data has shown that at least 0.2 mol.% of $Al_2O_3$ and $P_2O_5$ remain in their ordinary form near their equimolar concentrations and do not form an $AlPO_4$ join (the effect observed for all concentrations of $AlPO_4$ join from 5 to 25 mol.%).

**Keywords:** large mode area fibers; refractive index; phosphorosilicate glass; aluminosilicate glass; aluminophosphosilicate glass; $AlPO_4$ join; optical fiber design; fiber fabrication

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## 1. Introduction

High average and peak power fiber lasers require the utilization of large-mode-area (LMA) active optical fibers. The main demand for such fibers is the low numerical aperture (NA) of the core. For example, the NA of 0.04–0.07 is routinely used to achieve single-mode operation in kW class fiber lasers with a core diameter of ~20–30 μm [1–9]. Some of the fiber designs, like photonic-crystal fibers (PCFs), could provide an endless single-mode behavior, require an even lower core refractive index—it should be exactly equal to that of undoped silica cladding [10–15]. To achieve so small a level of the core NA, a careful control of dopants is required because rare-earth elements (such as $Yb^{3+}$ ions) have their own refractivity. Silica glass simultaneously doped with $Al_2O_3$ and $P_2O_5$ (APS glass) is one of the most promising solutions for the fabrication of LMA-active optical fibers. In APS glass, $Al^{3+}$ and $P^{5+}$ ions form an $AlPO_4$ join, which has refractive index close to that of silica [16–19]. This formation of the $AlPO_4$ join was confirmed in APS glass, i.e., by Raman spectroscopy [17]. Also, it was shown that the $AlPO_4$ join increases the solubility of rare-earth ions [20–22], which make it possible to create large-mode-area fibers with a high concentration of active dopants [3–9,15]. There are many papers devoted to the study of the APS glass refractive index [16,18,19,23], but all were conducted using measurements in fiber preforms or bulk materials. Our recent study has shown that the refractive index of the core could be noticeably (by more than 0.001) changed during drawing preform into optical fibers [24]. The effect becomes especially crucial near equimolar concentrations of $Al_2O_3$ and $P_2O_5$, where core-cladding refractive index difference could be changed even from

negative (in preform) to positive (in optical fiber) [24]. To date, there is still lack of papers devoted to the investigation of refractive index behaviors in APS optical fibers. Moreover, there are no precise data on the minimum refractive index, which could be obtained in the APS core in the fiber. For example, data provided in [24] for the refractive index of the $AlPO_4$ join have a variation of ~0.002. Such uncertainty is not acceptable for the design of LMA fibers, where the precise knowledge of the glass matrix refractive index is required to reveal the amount of active dopant that could be incorporated into the fiber core without exceeding the required core NA.

The aim of our current work was to determine the minimum refractive index in the optical fiber core made of APS glass and its dependence on the APS core compound. For this aim, a series of specially designed APS preforms with varying concentrations of $Al_2O_3$ and $P_2O_5$ were fabricated. The dependence of the APS glass refractive index on its compound near the equimolar concentrations of $Al_2O_3$ and $P_2O_5$ was determined with a high accuracy. A non-complete reaction of $Al^{3+}$ and $P^{5+}$ ions (which additionally increases core refractive index by ~0.0008) was reported for all $AlPO_4$ join concentrations (5–20 mol.%) near the equimolar $Al_2O_3$ and $P_2O_5$ contents.

## 2. Materials and Methods

Optical fiber preforms with APS core were fabricated using the conventional Modified Chemical Vapor Deposition (MCVD) method. All the dopants were deposited from the gas phase. As precursors, we used the low-boiling liquids $SiCl_4$, $POCl_3$, and $C_2F_3Cl_3$. For doping with $Al_2O_3$, we used $AlCl_3$ (99.999% purity on metals basis) as a precursor. On the contrary to other precursors, the $AlCl_3$ is a low-volatility solid under ordinary conditions, and, to achieve a high enough vapor pressure, it is necessary to heat it up to 125–140 °C. To realize such conditions, the MCVD set-up was equipped with a system for evaporation of $AlCl_3$ powder precursor. Vapor of $AlCl_3$, together with the carrier gas Ar, was delivered to the reaction zone using a separate heated line (to exclude a reaction with $POCl_3$ in the delivery line) until its mixture with other components inside the supporting tube. It is worth noting that stresses between the core and cladding due to differences in the thermal expansion coefficient could be very high for the highly doped core. So, special attention was paid during preform handling to exclude its cracking (for example, we avoided cutting the preform and tore it apart with a flame when it was necessary).

Refractive index profile (RIP) in preforms was measured using Photon Kinetics preform analyzer PK2600 by scanning the deflection of laser beam along the preform diameter. Each preform was measured at a few positions along an axis to confirm its uniformity. At each axis position, the measurements were performed for two or three different rotation angles around the preform axis, and then they were averaged. Refractive index repeatability for this set-up, specified by the supplier, is below 0.00005. However, absolute accuracy is defined by the calibration of this set-up, which is typically conducted using special calibration preform, and we estimate the relative error (which depends on value of measured difference between core glass refractive index and refractive index of the first cladding made of undoped silica glass) to be better than 3%. The measured refractive index difference in the studied preforms ranged from −0.003 to +0.003, so we estimate the absolute refractive index (more exactly, its difference relative to undoped silica glass) measurement accuracy to be 0.0001.

In our previous study [24], we demonstrated that refractive index profile in optical fiber could be noticeably changed from that of the fiber preform. By this reason, each fabricated preform was drawn into optical fiber with outer diameter of 125 μm. Core/clad ratio in the fabricated preforms was kept large enough (>1/4) to have core diameter of about 30–40 μm.

It is known that refractive index difference between core and cladding could be noticeably affected by fiber drawing conditions [25]—refractive index of undoped silica cladding is reduced with growth of drawing tension, and difference may reach 0.0014 when drawing tension exceeds 300 g. By this reason, special attention was paid to keep drawing tension below 30 g to reduce variation of refractive index of the undoped silica cladding on the level of less than 0.0002. For this aim, drawing temperature was kept to be reasonably high (~2000 °C). It was not changed for preforms with different compounds of the core as a main part of the preform (~90%) was formed by cladding made of undoped silica glass.

The spatial distribution of chemical elements was determined in the fiber samples with the help of energy-dispersive X-ray spectroscopy (EDXS) (JSM5910-LV, JEOL, Tokyo, Japan equipped with AZtecENERGY analytical systems, Oxford Instruments, Oxfordshire, UK). The analyses were performed in the fiber samples by scanning along the core diameter. The samples for the EDXS analysis were coated with a conducting carbon. To calibrate EDXS system, we used etalon based on $AlPO_4$ single crystal for calibration of a signal corresponding to P and Al atoms and undoped fused silica glass for calibration of a signal corresponding to Si atoms. It allowed us to increase accuracy of measurements due to similarity of etalons and studied glass samples. The analytical errors were estimated to be 0.09, 0.12, and 0.17 wt.% for Al, P, and Si respectively.

RIPs in the fabricated fibers were measured using refractive near field technique (fiber analyzer EXFO NR9200HR was used). Two perpendicular scans along the core diameter were made in each fiber, and the results were averaged to achieve the best accuracy of RIP determination. Both distributions (RIP and compound) were measured in optical fibers with resolutions better than 1 μm, which allowed us to compare refractive index and glass content at different radius positions (typically, 10–20 points with different $Al_2O_3$ and $P_2O_5$ ratio were measured in each fiber with step of ~1 μm). Accuracy of this method for measurements of refractive index in optical fibers (its difference relative to undoped silica glass) was specified by the equipment manufacturer to be about 0.0005. However, reproducibility, which is even more important for comparison of refractive index in different samples, is even higher and specified by the equipment manufacturer to be about 0.00015.

## 3. Results

To determine the minimum refractive index of the APS glass, a set of preforms with different concentrations of $Al_2O_3$ and $P_2O_5$ was fabricated and then drawn into the fibers. The core of each preform was doped non-uniformly along the radius—the ratio between the molar concentration of $Al_2O_3$ and $P_2O_5$ was continuously changed from P-excess at the outer layers to Al-excess in the central part of the core. As a result, each fiber at some radius had a layer with equal molar concentrations of $Al_2O_3$ and $P_2O_5$. The distribution of the dopants ($Al_2O_3$ and $P_2O_5$) and the measured RIPs in some of the above-mentioned fibers are shown in Figure 1a–d. The RIPs measured in the fiber preforms (and rescaled to the fiber dimension) are shown in the same figures for reference.

If we suggest a near complete reaction of $Al_2O_3 + P_2O_5 \rightarrow 2AlPO_4$, we could estimate the molar concentration of the $AlPO_4$ join as double the molar concentration of the dopants ($Al_2O_3$ or $P_2O_5$) that have the smallest concentration. Such an estimation of the $AlPO_4$ join concentration does not take into account the possible non-complete reaction of the $Al_2O_3$ and $P_2O_5$ reported in [18,23], but it simplifies the designation of fiber preforms with different concentrations of dopants. In such terms, the $AlPO_4$ join concentration in the fabricated preforms was changed from ~3 mol.% up to 25 mol.% to cover most of the interesting glass compounds.

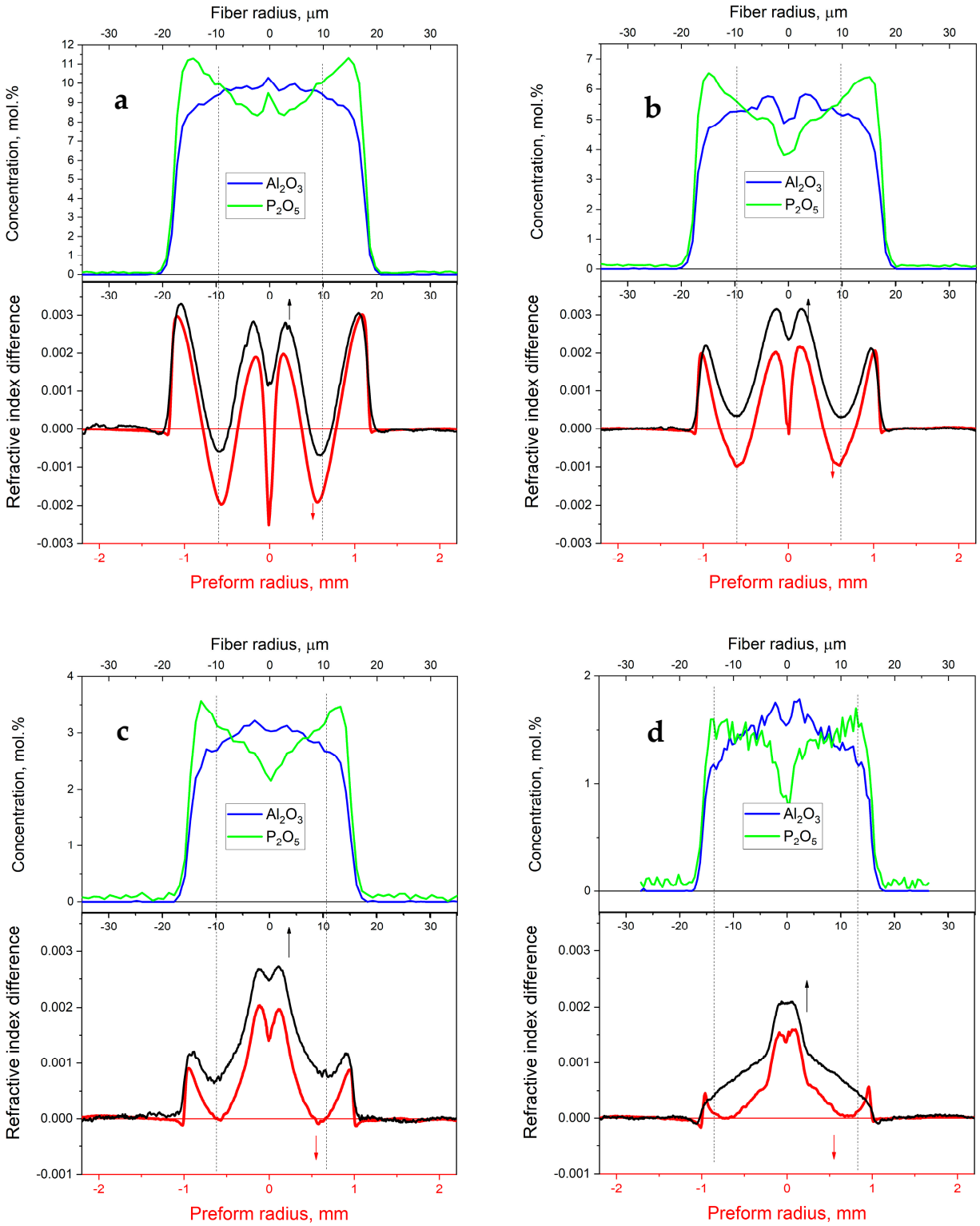


**Figure 1.** Distribution along the fiber radius of $Al_2O_3$ and $P_2O_5$ concentrations (upper part of each figure) and refractive index profile (its difference relative to undoped silica glass) in optical fiber and fiber preform (bottom part of each figure). Different figures correspond with samples with different concentrations of $AlPO_4$. (**a**): ~19 mol.% $AlPO_4$ (sample KS008); (**b**): ~10 mol.% $AlPO_4$ (sample KS007); (**c**): ~5 mol.% $AlPO_4$ (sample KS009); (**d**): ~3mol.% (sample KS010). RIP in the fiber preform (shown by red lines) was rescaled to match that of the drawn fiber (shown by black lines). Fiber dimension is shown by upper x-scale (indicated by black arrow), while down x-scale shows preform radius dimension (indicated by red arrow) for reference.

First, we defined the radial positions to correspond with a minimum refractive index in both the fiber preforms and optical fibers drawn from it. It is interesting to note that the measured concentration of $P_2O_5$ at these radii was slightly higher than the concentration of $Al_2O_3$. This feature was observed for all of the studied fibers. The difference was quite small (on the level of ~0.5 mol.%) and close to the inaccuracy of the concentration measurements.

Also, it could be seen that the refractive index in the core of studied preforms was smaller by ~0.001 than that of the optical fiber. This feature was first reported by our group in [24] and explained as a difference in the cooling conditions of the preforms (slow cooling in tens of minutes) and fibers ("shock" cooling in seconds) and, as consequence, the different impact of mechanical stress on the core refractive index.

The dependences of the minimum measured refractive index difference between the APS glass and undoped silica cladding measured in the fiber preforms and optical fibers drawn from it are shown in Figure 2 (in Figure 1, the corresponding positions are shown by dashed lines). For the fiber shown in Figure 1d with the smallest concentration of $AlPO_4$ (~2–3 mol.%), we used the refractive index value measured at a radius of 14 μm. In this fiber, there was no clear minimum of the refractive index (contrary to the fiber preform from which this fiber was drawn). We suggest that this might be due to the diffusion of phosphorous during the drawing of the fiber (and the decrease in its maximum content near the core-cladding interface). Nevertheless, it is clear that the minimum refractive index difference with the undoped silica level for such content of $AlPO_4$ does not exceed dn = 0.0004; we believe that this number is very close to the minimum value for this $AlPO_4$ join concentration.

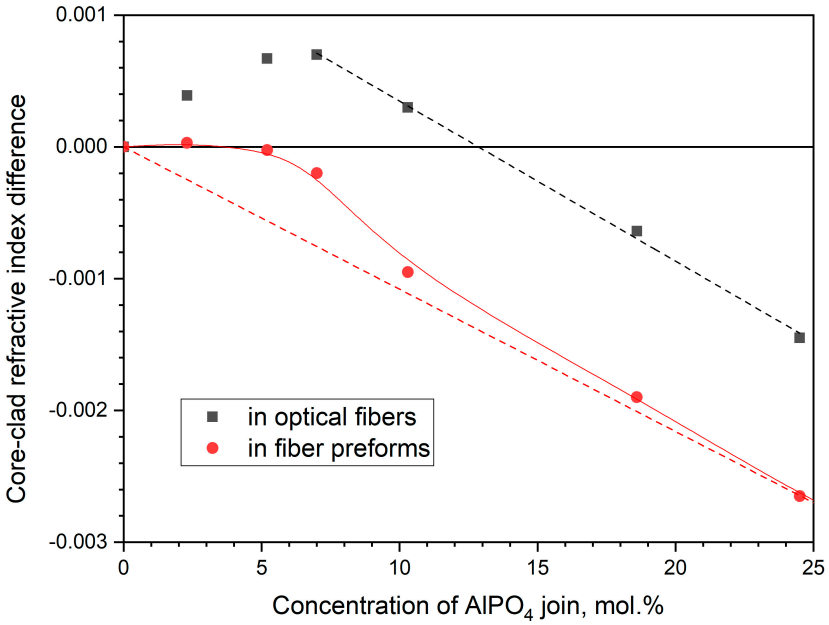


**Figure 2.** Dependance of minimum refractive index difference between APS glass and undoped silica cladding in optical fibers (black signs) and in fiber preforms (red signs). Red and black dashed lines show approximation given by Formular (1) and (2) correspondingly.

The dependences of the minimum refractive index on the $AlPO_4$ join concentration was found to be different in the fibers and in preforms. In the preforms for the $AlPO_4$ concentrations above 10 mol.%, the dependences tend to be linear with a slope similar to that reported in [14]:

$$\Delta n_{AlPO4} = n_{AlPO4} - n_{SiO2} = -0.108 \cdot 10^{-3} \cdot C_{AlPO4} \quad (1)$$

where $n_{AlPO4}$ is the estimated refractive index of the $SiO_2$-$AlPO_4$ glass (with a complete reaction of all of the available $Al^{3+}$ and $P^{5+}$ ions), and $n_{SiO2}$ is the refractive index of the undoped silica glass.

An increase in the refractive index relative to (1) was observed for preforms doped with $AlPO_4$ concentration in the range 2–10 mol.%. This effect was well described by the suggestion of a non-complete formation of the $AlPO_4$ join and the presence of some $Al_2O_3$ and $P_2O_5$ in its ordinary form [23]. In this case, the APS glass became a uniform mixture of $SiO_2$-$AlPO_4$ glass, $SiO_2$-$P_2O_5$, and $SiO_2$-$Al_2O_3$.

The behavior of the refractive index of the optical fibers is different to that in optical fiber preforms. It could be seen that for the $AlPO_4$ concentrations above 7 mol.%, the minimum difference between the refractive index of the APS core and undoped silica glass $\Delta n_{\mathrm{APS\_}fiber\_min}$ could be described by the following formula:

$$\Delta n_{\mathrm{APS\_}fiber\_min} = (1.56 \pm 0.06)\cdot 10^{-3} - (0.121 \pm 0.004)\cdot 10^{-3}\cdot C_{AlPO4}, \quad (2)$$

Approximation (2) does not provide $\Delta n_{\mathrm{APS\_}fiber\_min}$ equal to zero at $C_{AlPO4} = 0$, so it is quite natural that the dependence is broken at concentrations of $AlPO_4$ below 7 mol.%. It is expected that for a very small $AlPO_4$ concentration, the minimum refractive index of the APS glass must tend towards that of undoped silica glass. As could be seen in Figure 2, below 7 mol.% of the $AlPO_4$ join, this tendency is well observed. It is interesting to note that around 7 mol.% also, a maximum deviation of refractive index in preform from (1) is observed. We attribute this difference to a non-complete reaction of $Al_2O_3$ and $P_2O_5$, which is well described in [23].

The slope of dependance (2) is rather close (within 10% accuracy) to that of the $AlPO_4$ glass given by Formula (1). The most important difference between fibers and preform RIPs is the increase in the refractive index. The difference in the minimum refractive index in the fiber and preforms for the concentration of the $AlPO_4$ join above 10 mol.% is nearly constant and equal to 0.0012. For smaller concentrations of $AlPO_4$, the difference decreases near linearly with the concentration of $AlPO_4$. The change in tendency is caused by two effects—the rise in the refractive index in the preform caused by the non-complete formation of $AlPO_4$ [23] and the deviation of the fiber's minimum refractive index from the tendency described by (2).

The fibers in Figure 1a–c have both: regions with an excess of $Al_2O_3$ and an excess of $P_2O_5$ with a corresponding increase in the refractive index. This allows us to investigate the influence of excess $Al_2O_3$ and $P_2O_5$ concentration on the APS glass refractive index with a nearly equimolar content of dopants in a wide range of $AlPO_4$ join concentrations. To exclude the dependance of the refractive index on the $AlPO_4$ concentration in Figure 3, we have drawn an excess refractive index difference—the difference between the refractive index $n$ of the APS glass with an excess of $Al_2O_3$ or $P_2O_5$ and the nominal refractive index $n_{AlPO4}$ of $SiO_2$-$AlPO_4$ glass (with the same $AlPO_4$ concentration) defined by Formula (1). The resultant index difference, as a function of the difference in the nominal molar concentrations of $Al_2O_3$ or $P_2O_5$ (calculated without taking into account the formation of an $AlPO_4$ join), is shown in Figure 3a. It is interesting to note that in a wide range of $AlPO_4$ concentrations (5–20 mol.%), the dependences were found to be nearly identical within the accuracy of measurements. All of these dependences have a similar feature—the minimum of the optical refractive index is found for the molar concentration of $P_2O_5$ ($C_{P2O5}$) to be larger by ~0.45–0.55 mol.% than the concentration of $Al_2O_3$ ($C_{Al2O3}$) and not the equimolar concentration of $Al_2O_3$ and $P_2O_5$ ($C_{Al2O3} = C_{P2O5}$). Also, there is no sharp transition between Al-excess and P-excess, which should be observed in the case when all free $Al_2O_3$ and $P_2O_5$ form an $AlPO_4$ join. Instead, we could see a rather smooth transition, which indicates that some $Al_2O_3$ and $P_2O_5$ remain in their ordinary form and do not form $AlPO_4$.

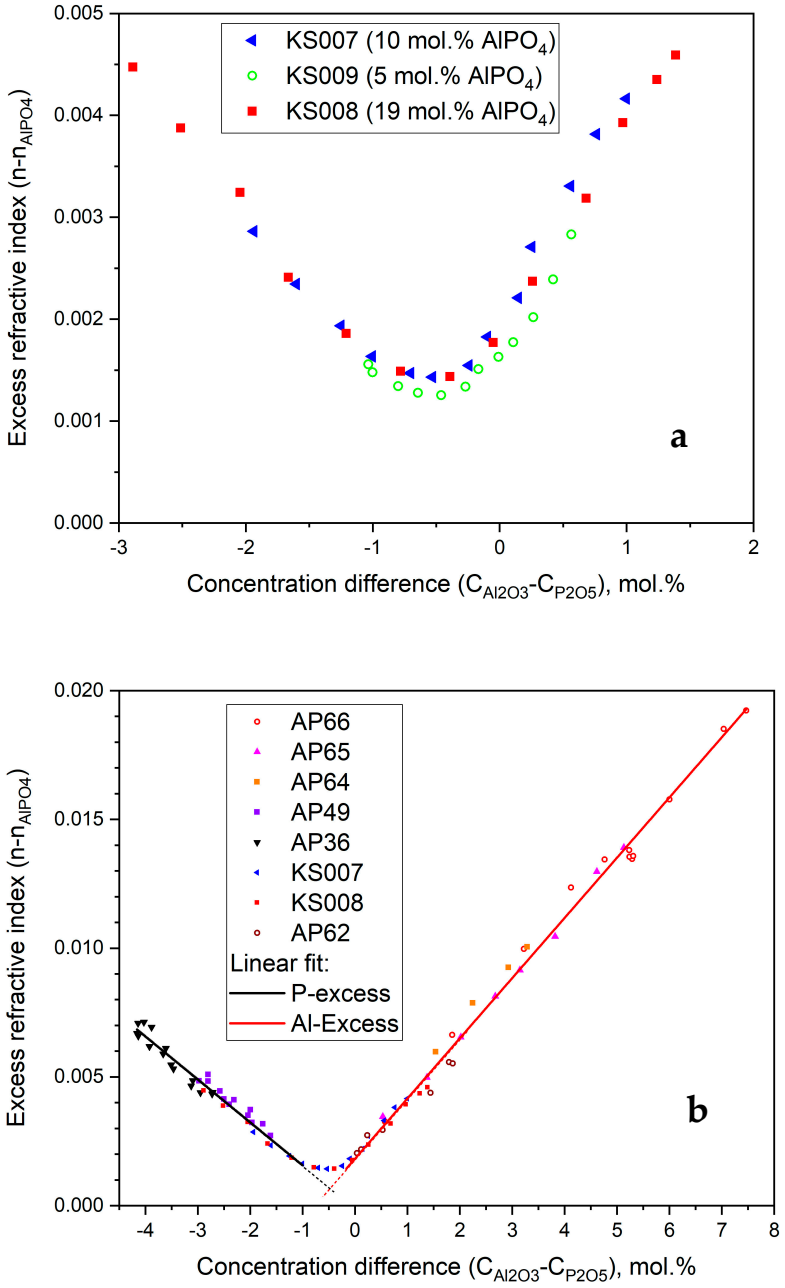


**Figure 3.** Dependance of excess refractive index of PAS glass (difference in its refractive index and nominal refractive index of $SiO_2$-$AlPO_4$ glass with the same content of $AlPO_4$ join, defined by Formula (1)). (**a**) Data obtained with fibers KS007, KS008, and KS009 having near equimolar content of $Al_2O_3$ and $P_2O_3$; (**b**): data obtaining all the fibers from Table 1, having content of $AlPO_4$ join 9–22 mol.%. Dashed lines show approximation of linear fit for P-excess and Al-excess regions to the region with minimum refractive index.

Data shown in Figure 3a allow us to conclude that the refractivity of the excess amount of $Al_2O_3$ and $P_2O_5$ are nearly the same in fibers with different concentrations of $AlPO_4$. However, the concentration range for data in Figure 3a is quite small, which might cause a relatively large error in the analysis of excess dopant refractivity. To solve this problem, we chose a limited concentration range of $AlPO_4$ (9–22 mol.%), which allowed us to exclude the fibers with non-linear dependances of the minimum refractive index on the $AlPO_4$ concentration (observed for $C_{AlPO4} < 7$ mol.%) and fiber where the crystallization of $AlPO_4$ might be observed ($C_{AlPO4}$ above 27–30 mol.%) [19,24]. All of the data are summarized in Figure 3b—each fiber is shown by its own color to demonstrate that the results obtained

using different fibers match each other with a reasonable accuracy. The dependance of the excess refractive index difference ($n - C_{AlPO4}$) on the excess molar concentration of $Al_2O_3$ or $P_2O_5$ ($C_{excessAl2O3} = C_{Al2O3} - C_{P2O5}$ for Al-rich APS glass and $C_{excessP2O5} = C_{P2O5} - C_{Al2O3}$ for P-rich APS glass) could be approximated by the following linear formulas below:

For $P_2O_5$ excess,

$$n \cdot n_{AlPO4} = (0.1 \pm 0.1) \cdot 10^{-3} + (1.67 \pm 0.05) \cdot 10^{-3} \cdot C_{excessP2O5} \quad (3)$$

For $Al_2O_3$ excess,

$$n - n_{AlPO4} = (1.8 \pm 0.1) \cdot 10^{-3} + (2.34 \pm 0.04) \cdot 10^{-3} \cdot C_{excessAl2O3} \quad (4)$$

It could be seen that the dispersion of different points in Figure 3 is very small—the slope of dependences (3) and (4), which provide the refractivity of the excess amount of $Al_2O_3$ and $P_2O_5$, is defined with a high accuracy (the mean square deviation is less than 3% of the approximated value).

**Table 1.** Characteristics of fibers shown in Figure 2.

| Fiber Name | $C_{AlPO4}$ (Concentration of $AlPO_4$), mol.% | $C_{excessAl2O3}$ (Excess of $Al_2O_3$), mol.% | $C_{excessP2O5}$ (Excess of $P_2O_5$), mol.% | Refractivity of Excess $Al_2O_3$, $10^{-3}$/mol.% | Refractivity of Excess $P_2O_5$, $10^{-3}$/mol.% |
|---|---|---|---|---|---|
| AP36 | 20–22 | - | 2.7–4.2 | - | 1.93 |
| AP49 | 13–16.5 | - | 1.6–3 | - | 1.64 |
| AP62 | 13–21 | 0.5–1.9 | - | 1.85 | - |
| AP64 | 13.5–15.5 | 1.5–3.3 | - | 2.31 | - |
| AP65 | 12–14 | 0.5–5 | - | 2.32 | - |
| AP66 | 13–16 | 0.5–7.5 | - | 2.25 | - |
| KS007 | 9–10.5 | 0–1 | 0–2 | 2.2 | 1.3 |
| KS008 | 16.5–19 | 0–14 | 0–3 | 2.0 | 1.47 |

## 4. Discussion

A detailed study of the refractive index behavior in APS glass near equimolar $Al_2O_3$ and $P_2O_5$ concentrations was made in the current work. It allows us to reveal the main features of APS glasses. One of the important results that must be taken into account during the design of the fibers based on the APS glass matrix is the significant (up to 0.0012) change of the refractive index of the APS glass after drawing fiber preform to the fiber. This feature was reported in our previous study, but, in the current work, it was studied in detail, i.e., for the first time—for APS glass with relatively small dopants ($Al_2O_3$ and $P_2O_5$) concentrations. To the best of our knowledge, the APS glass is the only glass in which a change of the refractive index after drawing the fiber is positive; usually for glass with a high thermal expansion coefficient ($P_2O_5$-$SiO_2$ or $B_2O_5$-$SiO_2$), this change is negative. It might be attributed to the complicated process of stress formation in the core, i.e., extra-high pressure in the core during the manufacturing process [26], which could result in different stresses in the core after the fiber is cooled down. In particular, we suggest that a positive refractive index change in APS glass is caused by the compressed stress of the core (contrary to other compounds, where the core is typically stretched due to the low thermal expansion coefficient of the surrounded pure silica cladding).

It was shown previously that most of the properties of APS glass are defined by co-dopant ($Al_2O_3$ or $P_2O_5$) being in excess (many properties of APS glass with $Al_2O_3$-excess are similar to that of $SiO_2$-$Al_2O_3$ glass, and many properties of APS glass with $P_2O_5$-excess are similar to $SiO_2$-$P_2O_5$) [19,27]. From this point of view, we expected to find the

refractivity of excess $Al_2O_3$ in the APS glass ($2.34 \cdot 10^{-3}$—see Equation (4)) to be very close to the refractivity of $Al_2O_3$ in the silica glass (~$2.2 \cdot 10^{-3}$/mol.%) [24]. However, this rule does not work for APS glass with $P_2O_5$-excess. The refractivity of the excess molar concentration of $P_2O_5$ ($1.67 \cdot 10^{-3}$/mol.%—see Equation (3)) is noticeably (almost twice) higher than the refractivity of $P_2O_5$ in the silica glass ($0.9 \cdot 10^{-3}$/mol.%) [24]. This discrepancy is much larger than the inaccuracy of our current measurements and approximations. For example, in the previous work [24], we define $P_2O_5$ excess refractivity $1.04 \cdot 10^{-3}$/mol.%, but there were only a few points in the P-excess region, and the dispersion of the data was very high due to the variation of the refractive index with an $AlPO_4$ concentration (in [24], the refractive index for $AlPO_4$ was not subtracted, in contrast to our current work, so an additional variation of the refractive index due to matrix $SiO_2$-$AlPO_4$ disturbs the data). Even if we consider each of the fibers from Figure 3a separately and approximate the refractive index dependence on the excess concentration (see the results presented in Table 1), we will obtain refractivity close to that defined by Equation (3) with large variations only for those samples (AP36 and AP62) where the concentration range is small (~1.5 mol.%). The smallest refractivity of excess $P_2O_5$ was $1.3 \cdot 10^{-3}$/mol.%—much larger than that in the binary phosphorosilicate glass. So, the change in $P_2O_5$ refractivity in the APS glass is significant and well above the accuracy of our measurements. Indeed, the difference in the refractivity of $P_2O_5$ in the pure silica glass and $P_2O_5$ in the APS glass become as high as $0.75 \cdot 10^{-3}$/mol.%, so, for the studied concentration range of $P_2O_5$ excess (up to 4 mol.%), the difference reaches 0.003—the value, which is almost an order in magnitude higher than the accuracy of refractive index measurements, equal to 0.0005 (specified in the Materials and Methods section). A similar effect was observed previously in the preform of APS optical fibers [19], where the refractivity of the excess molar concentration of $P_2O_5$ was found to be about $1.4 \cdot 10^{-3}$/mol.%. One possible reason for this effect is the different internal stresses in the core for the APS glass near the $AlPO_4$ and the APS glass with a high $P_2O_5$-excess.

It is worth paying attention to the behavior of the refractive index near the equimolar concentration of $Al_2O_3$ and $P_2O_5$. In the case of the reaction of all available $Al^{3+}$ and $P^{5+}$ atoms with the formation of an $AlPO_4$ join, the dependence refractive index on the difference in concentrations of $Al_2O_3$ and $P_2O_5$ must be V-like with a very sharp transition between $Al_2O_3$-excess and $P_2O_5$-excess regions (similar to that shown by the dashed lines in Figure 3b). In our case, this is not so; therefore, we could conclude that some $Al_2O_3$ and $P_2O_5$ remain in their ordinary form near the equimolar concentration. The minimum concentration of unreacted $Al_2O_3$ and $P_2O_5$ could be roughly estimated if we assume that the difference between the measured data of the refractive index and the linear approximations of the refractive index in $Al_2O_3$-excess and $P_2O_5$-excess regions (shown in Figure 3b by dashed curves) is due to the unreacted amount of $Al_2O_3$ and $P_2O_5$. The maximum refractive difference between these curves is about 0.0008; so, if we suggest that there are same molar concentrations of unreacted $Al_2O_3$ and $P_2O_5$ molecules and take into consideration its refractivity obtained in the current paper (Equations (3) and (4)), we could estimate the concentration of each dopant ($Al_2O_3$ and $P_2O_5$), which remains in their ordinary forms as ~0.2 mol.%. Real concentrations of unreacted dopants might be higher; our calculations give a low estimate.

It is worth noting that the minimum refractive index in the fiber core was achieved not for the position of equimolar concentration but for a small excess of $P_2O_5$ (~0.5 mol.%). It is interesting to note that a similar effect was reported previously in [28]. In this work, the minimum refractive index was found for the Al/P ratio of ~0.8 (for 1–3 mol.% of dopants), which, in absolute units, corresponds with a concentration difference of up to ~0.5 mol.% (similar to our results). It is not clear whether this effect is real (i.e., caused, for example,

by the non-complete reaction of $Al_2O_3$ and $P_2O_5$) or if this is just a measurement error. Indeed, the standard accuracy of our measurements (mean square deviation) estimated in the program used in EDXS is about 0.1 mol.% for both $Al_2O_3$ and $P_2O_5$. Thus, this inaccuracy could become twice larger (~0.2 mol.%) when we calculate the difference in the concentrations of $Al_2O_3$ and $P_2O_5$. This error might be a systematic error due to a background signal or noise. Indeed, in Figure 1, it could be seen that the concentration of $P_2O_5$ does not drop to the zero level at radii more than 20 μm. These radii correspond with Heraeus F300 supporting tubes, which does not contain $P_2O_5$ at all. This value seems to be an inaccuracy of the calculation method used in EDXS. It means that some systematic errors in the $P_2O_5$ determination of about 0.1–0.2 mol.% might be present in our measurements. So, one of the probable explanations of the observed refractive index's minimal shift from the equimolar concentration is the insufficient accuracy of the used EDXS method.

## 5. Conclusions

The study described in this work provides important data for the design of APS-active fibers with a low core NA. For the first time, the minimum refractive index achievable in the APS glass core of optical fibers was revealed for all concentration ranges of the $AlPO_4$ join. It was found that APS glasses with a concentration of an $AlPO_4$ join in excess of 14 mol.% could have a refractive index below that of the undoped silica cladding, which makes it suitable for the fabrication of active core in PCF fibers. Indeed, active dopants like $Yb_2O_3$ will increase the core refractive index, but it must be on the level of undoped silica cladding to be used in the PCF. Thus core glass matrix should have refractive index below that of the undoped silica to compensate positive refractivity of active dopant. Also, it is shown that the refractive index in optical fibers increases by 0.0004–0.0012 (depending on the $AlPO_4$ join concentration), which is relative to that measured in fiber preform. The refractivity of the excess amount of $Al_2O_3$ and $P_2O_5$ was also obtained with a good accuracy, i.e., the anomalous rise of $P_2O_5$ refractivity (relative to that in phosphosilicate glass) has been observed.

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