# THE PREPARATION OF $GeO_2$ - PbO GLASSES WITH LOW CONCENTRATION OF OH GROUPS

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*Glasses on base germanium dioxide, $GeO_2$, have a good optical transmission in near and middle infrared region of spectrum up to 4.5 μm. Various oxides, as PbO, $TeO_2$, etc. added to $GeO_2$ produce binary and ternary glasses having the similar optical properties as pure $GeO_2$ and they are more stable. This paper deals with the study of $GeO_2$ - PbO glassy system and with the preparation of these glasses having the low concentration of OH groups. The preparation of glasses was carried out under reactive chlorine atmosphere combined with the oxygen one. The concentration of OH groups is determined from the values of extinction coefficients calculated from the intensity of the absorption bands at the wavelength 2.93 μm. These glasses can be used for drawing of optical fibers usable for a power delivery of Er:YAG laser energy in medicine and for chemical sensors.*

## INTRODUCTION

Germanium dioxide, $GeO_2$ , glass has a good transmission in infrared region of spectrum up to 4.5 μm. Various modifiers as PbO, $TeO_2$ , $TiO_2$ , $Sb_2O_3$ , $Bi_2O_3$ and ZnO can be added to produce the glasses which are more stable and have similar infrared transmission [1]. Owing to their good optical properties, these glasses are progressive candidates in optoelectronics as optical fibers for power delivery of Ho:YAG (2.01 μm) and Er:YAG (2.93 μm) laser energies. The radiation of these lasers is very suitable for medical application due to the favourable values of the absorption coefficient of human tissue. The theoretical values of optical losses of glasses based on $GeO_2$ and $TeO_2$ are lower ($2 - 5 \times 10^{-2}$ dB $km^{-1}$ at 2.98 μm for $GeO_2$ and 5.4 μm for $TeO_2$) in the comparison with $SiO_2$ glasses [1].

### $GeO_2$ - PbO glasses

Lead oxide, PbO, is very suitable modifier and glasses containing up to 50 mol% PbO can be obtained [2,3].

The samples of the glasses were prepared by melting the mixture of oxides ($GeO_2$ and PbO) or carbonates in Pt, quartz, aluminia or other crucibles under air or nitrogen atmosphere at temperatures 900 to 1000 °C for 1 hour. The thickness of prepared samples was about 1.5 mm. In the near infrared region of spectrum very strong absorption band at 3600 $cm^{-1}$ (2,9 μm) belonging to the fundamental vibration of OH groups was found in all prepared glasses [4]. One of the main conditions of using optical fibers for the power delivery and sensor systems is high chemical and physical purity of prepared glasses, namely the very low concentration of impurities having absorption bands close to the wavelengths of the laser radiation and low concentration of scattering centers.

## EXPERIMENTAL PART

The research deals with the preparation of pure glasses of $(GeO_2)_{1-x}(PbO)_x$ composition with low concentration of OH groups. To make feasible the application of optical fibers from these glasses for power delivery of Er:YAG laser energy, the concentration of OH groups should be very low as the absorption band of OH bonds lies very near to the wavelength of Er:YAG laser radiation.

The extinction coefficient $\alpha = \ln(I_0/I) / d$ ($cm^{-1}$) involving the concentration of OH groups has been obtained to characterize the absorption at 2.93 μm. Here $I_0$ and $I$ are input and output intensities of the radiation and $d$ is the thickness of the sample.

### The preparation of $(GeO_2)_{1-x}(PbO)_x$ glasses

The glasses were prepared in the concentration interval for $x$ from 0.3 to 0.5 under the various technological conditions and in the reactive atmosphere (see Table I). The mixture of starting oxides was melted in Pt, MgO, BN and alumina crucibles. Chlorine reactive atmosphere was obtained by thermal decomposition of $CCl_4$ at the temperature 800 °C, nitrogen was evaporated from liquid $N_2$ and oxygen was dried by passing through molecular sieve. The schematic apparatus for the preparation of the glasses in the reactive atmosphere is given in Figure 1. The compositions of prepared glasses were determined by X-ray microprobe analysis (relative error ± 3%).

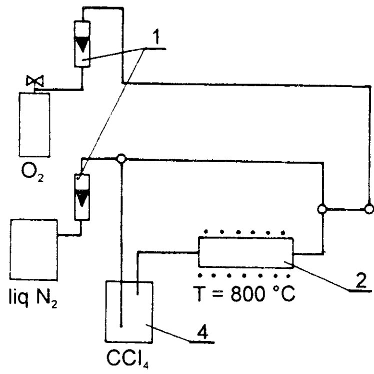


Figure 1. The schematic apparatus for the preparation of the glasses in the reactive atmosphere
1 - flowmeters; 2 - decomposition furnace; 3 - melting furnace; 4 - saturation chamber; 5 - sanitation of vapours

The exact measurements of the extinction coefficients should be carried out using the bigger samples and therefore the rods (preforms) were prepared by casting the glass melt (920 °C) into pre-heated form (300 - 400 °C). Samples were annealed to room temperature. The preforms, which can be used for the optical measurements of infrared absorption spectra and for fiber's drawing too, were 10 mm in diameter and 20 - 50 mm in length.

Table I. The conditions of glass preparation of $GeO_2$-PbO glasses (starting oxide materials)

| Condition | Atmosphere | Temperature (°C) | Time (min) |
|---|---|---|---|
| 1 | air | 550 | 60 |
| | | 890 | 60 |
| 2 | $N_2$ | 600 | 60 |
| | | 900 | |
| 3 | $N_2 + Cl_2$ | 500 | 15 |
| | $N_2 + Cl_2$ | 900 | 20 |
| | $O_2$ | 920 | 30 |
| 4 | $N_2$ | 450 | 15 |
| | $N_2 + Cl_2$ | 450 | 30 |
| | $N_2 + O_2$ | 450 | 15 |
| | $N_2 + O_2$ | 940 | 60 |
| 5 | $N_2$ | 450 | 15 |
| | $N_2 + Cl_2$ | 450 | 30 |
| | $N_2 + O_2$ | 450 | 15 |
| | $N_2 + O_2$ | 940 | 120 |

The infrared absorption spectra were measured in the region from 2 to 6 μm using Mattson 3000 Unicam Spectrometer. The thickness of the samples was from 2 to 5 mm, the diameter was about 10 mm. The surfaces of the samples were polished to have the optical quality.

## RESULTS AND DISCUSSION

The conditions of the glass preparation are given in Table I. The mixtures of starting oxides were melted in Pt, MgO, $Al_2O_3$, quartz and BN crucibles. Due to the partial interaction of the melt and crucible, the Pt crucible seems to be best. The samples were used for the optical measurements of infrared absorption spectra to calculate of the extinction coefficients at the wavelenght 2.93 μm. From the measurement of the infrared absorption spectra and from the calculation of the extinction coefficients it is seen that the reactive atmosphere influences very strongly the chemical and physical purity of the prepared glasses. Figure 2 and Table II indicate that the concentration of OH groups in the glasses under chlorine and oxygen atmosphere (condition 5) is by one order less comparing with that under air or nitrogen. The decrease of OH groups concentration can be attributed to their reaction with atomic chlorine. The presence of oxygen atmosphere during the last step of the melting is very important for removing so called "black particles" which can be explained by the presence of suboxides or metal

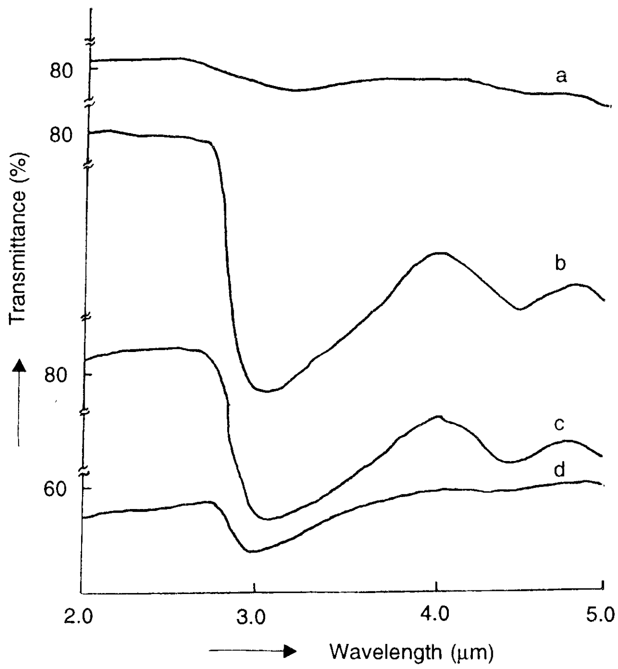


Figure 2. The infrared absorption spectra of $(GeO_2)_{0.6}(PbO)_{0.4}$ glasses prepared under various technological conditions
a - 5; b - 1; c - 3; d - 2 (1, 2, 3, 5 - conditions given in Table 1); Thicknesses of samples - 20 mm

particles coming from the process of the partial reduction during melting. These black particles can very strongly influence the scattering losses and the transmission of the samples.

Table II. The extinction coefficients of OH groups at 2.93 μm in $GeO_2$ - PbO glasses (60:40 mol%) prepared under various conditions (see Table I)

| No. | Starting oxides | Conditions of preparation | Extinction coefficient $\alpha=\ln(I_0/I)/d$ ($cm^{-1}$) |
|---|---|---|---|
| 1 | $GeO_2$, PbO | 1 | 2.76 |
| 2 | $GeO_2$, PbO | 2 | 2.13 |
| 3 | $GeO_2$, PbO | 3 | 1.76 |
| 4 | $GeO_2$, PbO | 4 | 0.47 |
| 5 | $GeO_2$, PbO | 4 | 0.47 |
| 6 | $GeO_2$, PbO | 5 | 0.25 |

## CONCLUSION

The heavy metal oxides combined with the base system $GeO_2$ or $TeO_3$ shift the infrared multifonone absorption due to the vibration of Ge-O bond to the longer wavelengths. This is the reason of higher transmissivity of the system in infrared region. The preparation of the glass under chlorine and subsequently oxygen atmosphere seems to be very effective for the diminishing the concentration of OH groups and the scattering losses. By this way it is possible to prepare preforms for fiber's drawing with low concentration of OH groups being suitable for the power delivery of Er:YAG lasers.

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## PŘÍPRAVA $GeO_2$ - PbO SKEL S NÍZKOU KONCENTRACÍ OH SKUPIN

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Oxid germaničitý, $GeO_2$, s různými jinými oxidy těžkých kovů jako PbO, $TeO_2$ a pod. tvoří stabilní skla s výbornou optickou propustností v blízké a střední infračervené oblasti spektra do 4.5 μm. Teoretické hodnoty optických ztrát těchto skel jsou 2 - $5.10^{-2}$ dB $km^{-1}$ a proto se jeví jako perspektivní materiály pro optická vlákna. Oxid olovnatý s $GeO_2$ tvoří širokou oblast skel až do 50 mol% PbO. Pro použití těchto skel v infračervené optice a optoelektronice je nutné, aby koncentrace OH skupin v připravených sklech byla co nejnižší, protože absorpční pas těchto skupin se vyskytuje u vlnové délky 2.93 μm, která prakticky odpovídá vlnové délce záření Er:YAG laseru. V článku je popsána příprava uvedených skel tavením výchozích oxidů v Pt kelímku v různých reakčních atmosférách. Optimální atmosférou k odstranění OH skupin se jeví atmosféra atomárního chloru, která je získána termickým rozkladem $CCl_4$ a k odstranění heteročástic (tzv. černé body) se osvědčila kyslíková atmosféra. Koncentrace OH skupin ve skle byla vztažena na hodnotu extinkčního koeficientu u vlnové délky 2,93 μm vypočteného z intenzity absorpčního pásu u této vlnové délky. Nejlepší výsledky byly získány kombinací reaktivní atmosféry chloru a kyslíku. Připravená skla jsou vhodná k tažení optických vláken přenášející záření Er:YAG laseru.