THE PREPARATION OF CHALCOGENIDE GLASSES IN CHLORINE REACTIVE ATMOSPHERE

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The preparation of chalcogenide glasses of high chemical and physical purity for their usage as optical fibers for optoelectronics was carried out by melting the starting materials in the reactive atmosphere generated by the thermal decomposition of various chloride compounds such as $TeCl_4$, $GaCl_3$, CCl_4, SCl_2 *etc.. This method is very effective for reducing the concentration of hydride (OH, SH, SeH groups) and oxide impurities in prepared glasses below* 10^{-4} *mol.%.*

INTRODUCTION

Many applications in medicine, chemical and biomedical sensors, ecology and industry demand optical fibers operating in middle and far infrared region of the spectrum [1]. Chalcogenide glasses belong to attractive materials for these applications and opposite to halide crystals and fluoride glassy fibers have many advantages. They have high chemical stability and durability and they are transparent in the spectral interval from 0.5 μm (for sulphide composition) to 20 μm (for telluride ones) [2].

The values of their theoretical optical losses calculated from the dependence of Rayleigh scattering and multiphonone absorption are app. 5×10^{-2} dB km^{-1} at 4.5 μm (sulphide), 6.15 μm (selenide) and 8.7 μm (telluride) [3] but at present the optical losses prepared fibers are about 0.1 dB m^{-1}.

The main reason of high optical losses is insufficient degree of chemical and physical purity. The chemical purity of glasses is given by the concentration of chemical impurities having absorption bands in the range from 0.5 to 20 μm and physical purity is connected to the amount of the physical defects causing scattering of the radiation. Both sources of impurities increase extrinsic losses of the radiation.

The required purity of prepared glasses is achieved step by step for many years due to very difficult problems with removing hydride, oxide and carbon impurities and physical imperfections such as bubbles, microcrystals and microparticles.

The impurities in the chalcogenide glasses causing extrinsic absorption can be divided into three categories:

- hydride impurities bring the absorption bands in the spectral interval of 2 - 6 μm corresponding to the vibration of the hydride bonds, such as SH (4.01 μm), SeH (4.57 μm), OH (2.92 μm), H_2O (6.30 μm).
- oxide impurities with absorption bands in the spectral range from 8 to 12 μm correspond to the presence of Se - O, As - O, Ge - O and Si - O bonds.
- carbon impurities exhibit the absorption in the spectral range from 5 to 8 μm due to the presence of CO_2, CO, hydrocarbonates, organic sulphide and selenide compounds.

These impurities can be introduced into the glass as from starting substances as from vapours of vacuum oil pump and also from inside residual atmosphere in an apparatus.

Scattering optical losses are introduced by heterophase impurities, inclusions, phase separation, bubbles etc. The decrease of the optical transmission is observed in the whole interval of infrared spectrum. The existence of these defects is strongly affected by the interaction of melts with the quartz apparatus, by the concentration of volatile impurities, by technological procedures etc.

To achieve the values of the optical losses of the chalcogenide glasses near the theoretical ones, the concentration of the hydride impurities should be about 10^{-6} at.%, oxide and carbon impurities have acceptable level about 10^{-5} at.%. The concentration of heterophase defects should be about 60 particles per cm^3 with a diameter of 5 μm and approx. 10^3 per cm^3 with a diameter of 0.5 μm. It can be achieved only by improving purification methods and technological procedures of glass preparation.

EXPERIMENTAL PART

The designed method for the reduction of the impurity concentration is based on the preparation of the glass under reactive atmosphere of halogen vapours generated by the thermal decomposition of halide compounds. The efficiency of the purification is followed by the measurements of the infrared absorption spectra and scattering.

Preparation of glasses

Purification of Se and S

Chalcogenide elements as probably the major source of hydride and carbon impurities should be re-purified before the glass synthesis. The distillation and the sublimation in the reactive chlorine atmosphere generated by the thermal decomposition of CCl_4, SCl_2, Se_2Cl_2, or in I_2 vapours seems to be more effective than the distillation under vacuum or in inert or hydrogen atmosphere. The distillation of Se is carried out at the temperature 650 °C, the sublimation of S at 550 °C.

Purification of glasses

This technological procedure involves the synthesis in reactive atmosphere, the distillation of prepared glasses and the preform preparation in the special ampoule. The connection of all technological procedures in the one apparatus lowers the possible contamination (namely by air) during the preparation procedures. This method is based on the principle of melting the glass in reactive atmosphere and the distillation under vacuum in the special ampoule (figure 1). Schematic technological procedures are as follows:

a) starting elements (approx. 30 g) and the halide compound (0.01 to 0.5 at.%) are inserted in the part A and after the evacuation and heating (330 °C), the seal S1 is made.
b) the synthesis of glass is carried out in the part A in reactive atmosphere due to thermal decomposition according to this equation: $MCl_2 \rightarrow M + 2Cl^{\cdot}$ of the halide compound. The melting temperature is 750 °C, melting time 8 hours.
c) the part D is evacuated and heated to remove moisture traces adsorbed on walls of the ampoules and then the brittle wall B is broken by quartz rod C.
d) the prepared glass is distilled under vacuum in open system from the part A to the part D at the temperatures 600 - 650 °C. Then the seal S2 is made and the parts A and D are separated by the seal S3.
e) the preform preparation is carried out in the part D by remelting and refining of the glass (750 °C), cooling and annealing. Prepared preforms are 80 - 100 mm in length and 12 mm in diameter.

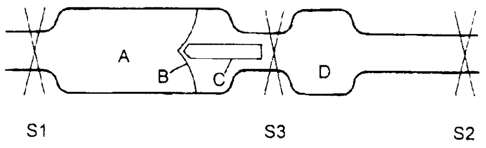

Figure 1. Special ampoule for the preparation of chalcogenide glasses in reactive atmosphere.
A - part for synthesis of glass in a reactive atmosphere; B - brittle wall separating both partes; C - quartz rod for breaking the brittle wall; D - part for distilled glass and preforming in preforms.

The reactive atmosphere

The reactive chlorine atmosphere in the part A (figure 1) is generated by the thermal decomposition of various halide compounds, such as $CaCl_2$, $AlCl_3$, $GaCl_3$, $InCl_3$, $PrCl_3$, $TeCl_4$ etc. according to above mentioned equation. The values of the free energy of ΔG of the thermal decomposition of some chloride compounds are given in table 1. The use of these compounds has two advantages - atomic chlorine $Cl^{\cdot}$ evolved during the synthesis reacts with hydride impurities and free metal serves as getter and reacts with oxides. Therefore, the halide compound can remove both hydride and oxide impurities. After the distillation of the residual non-volatile chloride compounds, oxides and elemental carbon remains in the part A and volatile by-products originated by the reaction with atomic chlorine are removed by the evacuation of the ampoule before sealing.

Table 1. Free energies ΔG of the thermal decomposition of some chloride compounds (T = 1000 K) [5].

compound	ΔG (kJ mol^{-1})
CCl_4	-36.76
SCl_2	26.95
$SeCl_2$	52.54
$TeCl_4$	97.12
$GaCl_3$	376.52
$InCl_3$	317.52
$AlCl_3$	533.7
$CaCl_2$	642.0

Distillation of glasses
in the reactive atmosphere in an open system

The distillation of polluted glasses is also carried out in open system under the reactive chlorine atmosphere. The reactive chlorine atmosphere is obtained by the thermal decomposition of CCl_4 or SCl_2 in separate furnace at the temperatures 700 - 800 °C. The distillation of glass is carried out in the flow of the gas mixture of nitrogen and chlorine (20 mol.%) at the temperature 650 °C. After the distillation the part with pre-distilled glass is evacuated and remelted at the same conditions as before.

Absorption measurements

The infrared absorption spectra are measured on Mattson 3000 Unicam Spectrometer in the range 2.0 - 20 μm. The extrinsic scattering of sulphide and sulphide-selenide glasses is measured by He - Ne laser beam. The optical scattering is detected on the screen placed cca 50 cm from the end of the sample [3].

The concentrations of SH, SeH and OH groups are calculated from the intensity of the absorption bands at 4.01, 4.57 and 2.92 μm using the absorption coefficient 54 cm^{-1} $(at.\%)^{-1}$ for SH, 23 cm^{-1} $(at.\%)^{-1}$ for SeH and 91 cm^{-1} $(at.\%)^{-1}$ for OH group[4].

RESULTS

Purification od Se and S

Infrared absorption spectra of Se before and after distillation are given in figure 2. The concentration of SeH groups 10^{-6} at.% is about two orders lower than before distillation. Similar effect of the purification is found at the sublimation of S in chlorine atmosphere, where the concentration of SH groups is estimated to be about 5.10^{-6} at.%.

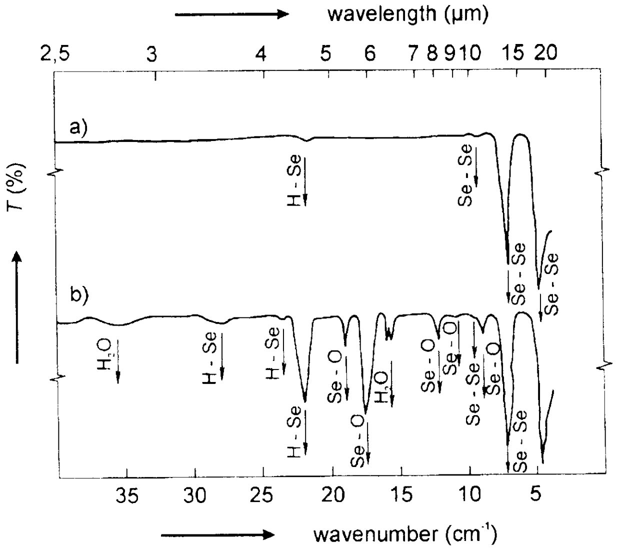

Figure 2. Infrared absorption spectra of selenium.
a) after purification; *b*) before purification.

The influence of the reactive halogen atmosphere on the concentration of impurities

The survey of the absorption bands and their intensities in the infrared absorption spectra of prepared chalcogenide glasses by melting with various the chloride compounds is given in table 2. The following experiences were obtained:

- very effective compounds for removing hydride impurities from As - S, As - Se, As - S - Se glasses seem to be $TeCl_4$ and then $AlCl_3$. In the infrared absorption spectra of the prepared samples only very weak absorption of SH or SeH groups are observed. The absorption band at 2.92 μm belonging to the OH group absorption is not detected.
- smaller effect of the purification was found using $GaCl_3$, $InCl_3$ and $PrCl_3$. In this case partial removing of the concentration of SH, SeH and OH groups is occured too, but their concentration is about one order higher.
- bromine and iodine vapours have less affectivity of the purification than chlorine reactive atmosphere.
- the distillation of glasses in open system in the flow of reactive gas atmosphere (Cl^- + N_2 + CCl_4 or SCl_2) is very effective for the removing of hydride impurities. The disadvantage of this method is the pollution of glasses due to the solubility of the reactive gases into glass melts and therefore after the distillation the glass has to be heated and remelted under the vacuum. The results are shown in figure 3.

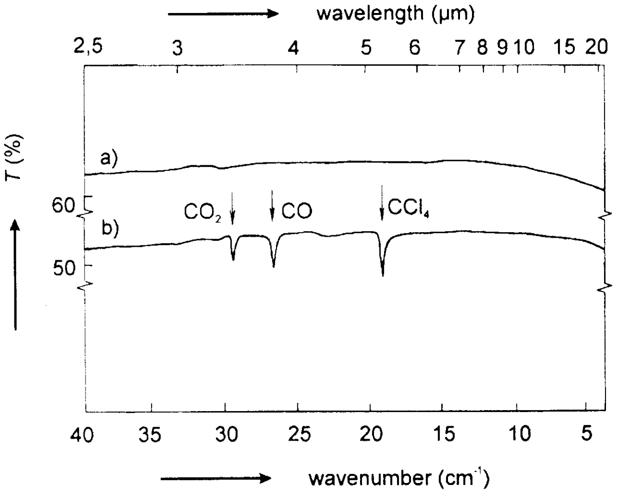

Figure 3. Infrared absorption spectra of glasses As_2Se_3.
a) after distillation in N_2 + Cl + CCl_4 atmosphere; *b*) after vacuum heating and remelting. Thickness of samples - 80 mm.

Table 2. Absorption bands and their intensities of impurities in chalcogenide glasses prepared under the reactive chlorine atmosphere. The concentration of impurities was calculated from the intensity of present absorption bands. Thickness of samples - 80 mm.

		absorption bands		
composition of glasses	reactive atmosphere	OH (2.92 μm)	SH (4.01 μm)	SeH (4.57 μm)
As_2S_3	$TeCl_4$	-	v. w.	
	$AlCl_3$	v. w.	v. w.	
	$PrCl_3$	w.	w.	
	$GaCl_3$	w. - m.	m. - s.	
	SCl_2	-	e. w.	
	CCl_4	-	v. w.	
	vacuum	s.	s.	
As_2Se_3	$TeCl_4$	-		e. w.
	$AlCl_3$	v. w.		v. w.
	$GaCl_3$	m.		m.
	CCl_4	-		e. w.
As_2S_2S	$TeCl_4$	-	e. w.	e. w.
	$AlCl_3$	v. w.	w.	v. w.
	$GaCl_3$	m.		s.
	CCl_4	-	v. w.	e. w.
	SCl_2	-	v. w.	-

e. w. – extremely weak - concentration ≈ 10^{-5} at.%
v. w. – very weak - concentration ≈ 10^{-5} - 7×10^{-5} at.%
w. – weak - concentration ≈ 7×10^{-5} - 3×10^{-4} at.%
m. – medium - concentration ≈ 3×10^{-4} - 10^{-3} at.%
s. – strong - concentration ≈ < 10^{-3} at.%

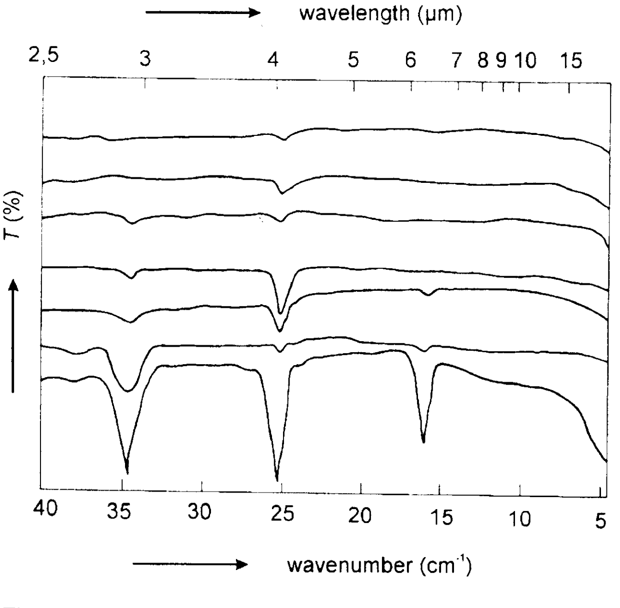

Figure 4. Infrared absorption spectra prepared in reactive atmosphere generated by various halogenide compounds and intensities of absorption bands present in glass.
a) - $TeCl_4$; *b)* - $AlCl_3$; *c)* - SCl_2; *d)* - $CaCl_2$; *e)* - $PrCl_3$; $PrCl_3$; *f)* - $GaCl_3$; *g)* - N_2.

The comparison of the infrared absorption spectra of the prepared glasses using the various reaction getters is shown in figure 4.

Scattering defects in glasses

Microbubbles are the main source of scattering losses in chalcogenide glasses. Their origin and concentration can be related to the concentration of volatile impurities as CO, CO_2, SH, SeH, CCl_4 etc. [3].

CONCLUSION

The chloride compounds as getter substances seem to be very advantageous as their thermal decomposition during synthesis results in production of the atomic chlorine reacting with hydride impurities and of the metal which reacts with oxide impurities. The best results were obtained with $TeCl_4$. Very effective purification of the glasses is the distillation under the chlorine atmosphere generated by the thermal decomposition of CCl_4 or SCl_2. Scattering losses are closely connected to the concentration of the volatile impurities. This confirms the fact that these impurities are soluble in the glass melt at higher temperatures. The decrease of their solubility with decreasing the temperature brings about the production of the microbubbles in studied glasses.

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PŘÍPRAVA CHALKOGENIDOVÝCH SKEL V REAKTIVNÍ ATMOSFÉŘE CHLORU

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Chalkogenidová skla tvoří velmi širokou skupinu neoxidových skel, chemicky a teplotně stabilních s výbornou optickou propustností záření ve střední a vzdálené infračervené oblasti spektra od 2 do 25 µm. Mezi nejvíce studovanými jsou skla o složení As_2S_3, As_2Se_3 apod., která jsou vhodná na tažení optických vláken pro přenos záření Er:YAG (2,97 µm), CO (5,3 µm) a CO_2 laserů. Pozornost v tomto článku je zejména zaměřena na přípravu vysoce čistých skel pro přenos záření Er:YAG a CO laseru, které má široké využití v medicíně, chemických a biomedicínských senzorech. Hlavní podmínka pro uvedené použití je příprava základních skel s vysokou chemickou a fyzikální čistotou, zejména s velmi nízkou koncentrací tzv. "hydridových nečistot" jako jsou OH, SH nebo SeH skupiny jejichž absorpční pásy se vyskytují u 2,93_µm, 4,01_µm nebo 4,58_µm. K odstranění těchto nečistot byla vyvinuta nová metodika, která umožňuje přípravu základních skel v reaktivní atmosféře, jejich destilaci a přípravy preformy v jedné speciální aparatuře. Reaktivní atmosféra, v tomto případě atomární chlor, vzniká během tavení skla rozkladem chloridové sloučeniny, která je přidána v definovaném množství k výchozím prvkům. V našem případě byla odzkoušena účinnost čištění těchto látek: SCl_2, Se_2Cl_2, $TeCl_4$, $AlCl_3$, apod. Při teplotě tavení skloviny dochází k tepelnému rozkladu uvedených sloučenin za vzniku atomárního chloru, který reaguje s OH, SH či SeH skupinami za vzniku HCl, který se následující destilací získaného skla odstraní. Efektivnost čištění byla určována z intenzity absorpčních pásů uvedených skupin a jako nejvhodnější se jeví SCl_2 a Se_2Cl_2 pro otevřené systémy a $TeCl_4$ pro uzavřené systémy. Koncentrace hydridových nečistot OH a SH skupin v připravených sklech je na a pod hranicí 10^{-4} at.%.