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CHALCOGENIDE GLASSES - SURVEY AND PROGRESS

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Chalcogenide glasses are reviewed. The physical properties are discussed in relation to the purity of the glass. The photo-luminescence properties and the state-of-art of applications are presented.

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1. Introduction

Articles from glasses have been produced already in old Egypt but, in spite of the huge progress in glass science up to-day, the glass is a material still poorly understood.

Most studies about glasses and their applications were carried out on silicate and quartz glasses, which transmit the radiation in visible range of the electromagnetic spectra. The application in optics, photonic, optoelectronics increased the demand in glasses which can transmit a radiation in infrared range up to the wavelength of ~ 2 µm. The chemical and physical properties of these, so-called, special glasses will complete the ones of silicate glasses. The limit wavelengths of the optical transmission for SiO_2 and for special glasses are shown in Fig. 1.

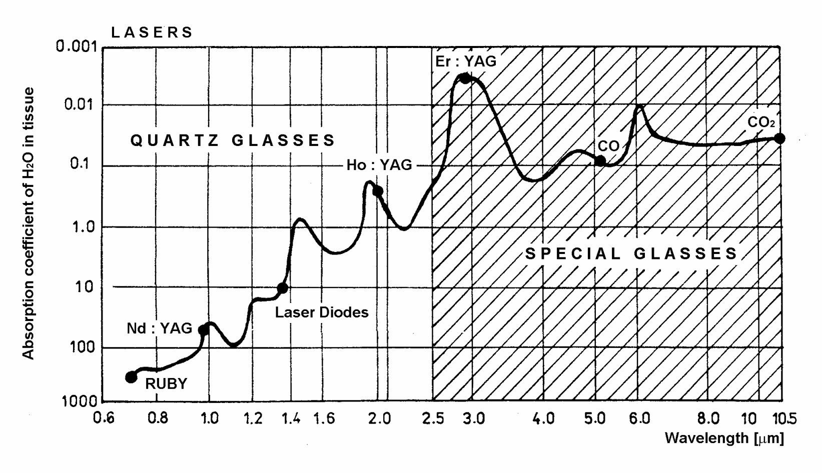

Fig. 1. The limit wavelengths of the optical absorption for SiO_2 and special glasses.

A general overview on special glasses is sketched in Fig. 2. The special glasses can be divided into three groups:

- Fluoride glasses based on ZrF_4 or HfF_4

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- Chalcogenide glasses – glasses based on chalcogens (S, Se, Te): e.g. As-S, As-Se, Ge-Ga-S, Ge-Ga-As-S, Ge-As-Se, Ge-Se-Te, As-Se-Te.
- Heavy metal oxide (HMO) glasses: e.g. – GeO_2-PbO, TeO_2-PbO, PbCl2, TeO_2 – ZnO, Ga_2O_3-PbO –Bi_2O_3, etc.

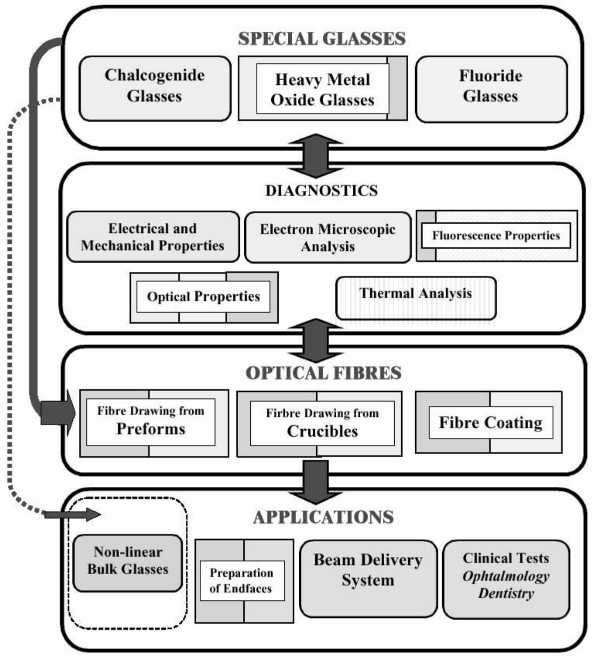

Fig. 2. Survey of special glasses – synthetic view.

The research on special glasses includes several steps beginning with the preparation procedures of high purity glasses, thereafter diagnostic of their properties (chemical, and physical properties), because the quality of prepared glasses influence their properties, and, finally, applications [1]. Glasses which fulfil necessary chemical and physical requirements are used to draw optical fibers [2]. Many fundamental studies and experiments are required for implementing the applications of special glasses as active or passive elements in those cases where silicate glasses cannot be used or their properties are not convenient.

This paper will be focused on the survey of the state of art in chalcogenide glasses, preparation of high purity, undoped and active glasses, of glasses doped with rare earth ions (RE^{3+}), their physico-chemical properties and applications.

2. The chalcogenide glasses

Chalcogenide glasses are solids with covalent bonds, the maximum fraction of ionic bonds being 9 %. They belong to the group of non-oxide glasses. This group of glasses has very different properties, if compared to oxide glasses, namely SiO_2 and silicates. Lucovsky [3] presented a classification scheme for high-k dielectrics that separates SiO_2 and the alternative non-crystalline dielectrics into three groups with qualitative different amorphous bonding morphologies.

Chalcogenide glasses contain one or more chalcogen elements, sulphur, selenium or tellurium, in a combination with other elements namely from IV-th, V-th and VI-th group of the periodical table.

First research on chalcogenide glasses in 1950, was focused on As_2S_3, an optical material for near and middle infrared region of the electromagnetic spectrum. In 1960, there were studied the electrical properties of some chalcogenide glasses and Kolomiets, Eaton, Ovshinsky and Pearson [4-7] observed their semiconductor properties and switching phenomenon.

At the beginning of ‘70 the research was split in two directions: the first one was dedicated to the optical materials for middle and far infrared region of the electromagnetic spectrum (for example As_2Se_3, Ge-As-Se, Ge-Se-Te) and, the second one was dedicated to the materials exhibiting threshold and memory switching phenomenon (this direction started with amorphous layers containing tellurium).

Today the attention is paid to the study of infrared optical fibers for the transmission of radiation and power delivery of Er: YAG, CO and CO_2 lasers, active laser fiber, and non-linear optics.

Among chalcogen elements only selenium and sulphur can be prepared in glassy state. Tellurium cannot be prepared in glassy form by cooling the melt. It can be obtained only as thin amorphous layer by deposition methods.

3. The preparation and purification of chalcogenide glasses

Chalcogenide glasses can be prepared by various ways both from the liquid and from the vapour phase. Most known methods are: cooling of melt, sol-gel [8], chemical vapour deposition, evaporation and sputtering [1]. Bulk glasses are mostly prepared by cooling of melts and partly by sol-gel method [8].

The CVD methods are mostly used for the preparation of glassy thin layers. Modified chemical vapour deposition method (MOCVD) has been developed for the preparation of preforms for fibre's drawing. The evaporation or the sputtering is used for the preparation of thin layers for switching devices, xerography, lithography, memory films.

A very difficult but very important problem is the preparation of high purity glasses, namely, without chemical and physical impurities. The avoiding of oxide, hydride, carbon or carbonate impurities and various physical defects: cracks, microcrystalline phase segregation etc. is important because these impurities and defects strongly influence the optical properties (transmission, scattering etc.), the solubility of rare earth ions, and other properties. The applications in optoelectronics demand high chemical and physical purity of the glasses [10]. The chemical purity is determined by the concentration of chemical impurities, while physical purity is defined by the concentration of physical defects as: heterogeneous particles, microcrystalline phase separation, cracks, inhomogenities etc. Chemical impurities cause the extrinsic absorption of radiation, while physical defects cause the scattering radiation. In order to approach the values of optical losses to the theoretical ones the concentration of impurities should be 10^{-5} mol% for hydrides, 10^{-6} mol% for oxides, 5×10^{-5} mol% for silicon and carbon, while the concentration of the physical defects should be about 10^2 -10^3 cm^{-3}. For this reason new advanced purification and preparation procedures were developed [11]. Chalcogenide glasses belong to substances which have an incongruent melting point, exhibit a high partial vapour pressure during melting and are susceptible to oxidation and hydrolysis and, therefore, the synthesis must be carried out in sealed evacuated quartz ampoules. The synthesis conditions are widely varied - they depend on the glass composition, glass-forming region, and glass forming ability. Thus, the glasses containing arsenic can be prepared at a temperature situated in the range 700 - 750 ^oC, the glasses with germanium are melted at 900 – 950 ^oC, while silicon melts at the temperature of 1150 ^oC. Further increase of the temperature of synthesis is limited by the softening temperature of quartz ampoule, which is around 1200 - 1250 ^oC.

The melt-cooling regime is also very dependent on the glass forming ability of the system. The melt can be cooled slowly (self-cooling furnace) for good stable glasses (As_2S_3 , As_2Se_3). Faster cooling rates (quenching) for unstable glasses can be achieved by cooling in air or by plunging the sealed ampoule into cold water or even liquid nitrogen (telluride). The temperature of annealing is very important.

To achieve the value of the chemical purity suitable for power delivery of laser energy and for the preparation of active and laser fibers doped with rare earth ions (Pr, Er, Dy, Nd etc.) new methods have been developed because in glasses prepared only by direct synthesis from starting elements the average concentration of hydride and oxide impurities is around 10^{-3} mol% and the physical defects around 10^4 cm^{-3}.

The purification of the glasses must be done in many steps, namely, before the synthesis and during synthesis (Fig. 3). The major sources of impurities seem to be the starting elements S, Se, Te, As, Ge, Ga etc. and, therefore, volatile elements are re-purified by sublimation in reactive atmosphere (SCl_2) or under vacuum (part A). Ge, Ga etc. are melted in a high vacuum at the temperature about of 950 ^oC (part D). The technological procedures involve the distillation of S or Se or As (from A to D), the synthesis of the undoped or doped glasses, and the preparation preforms for fibre's drawing. All these operations are carried out in special quartz ampoules (part D) (Fig. 3) [12, 13]. This arrangement diminishes the danger of contamination of the laboratory atmosphere during the preparation procedure. Thus, undoped and doped glass preforms or rods with 10 mm in diameter and 100 mm in length were obtained. Detailed technological procedure is given in paper [14]. The special quartz ampoule consists from part A (for purification), B - brittle wall separating both parts, C - rod for breaking brittle wall, D - part for synthesis of glasses and preforms, S1, S2, S3 - vacuum seals, as seen in Fig. 3.

For the study of the properties and quality of prepared glasses various diagnostic methods were used. They are shown in Fig. 2.

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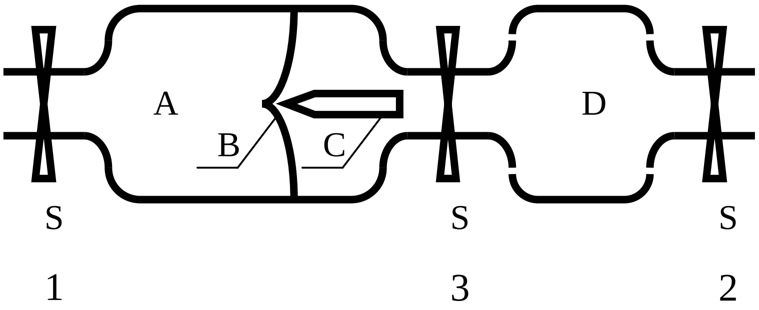


Fig. 3. Special quartz ampoule device for glass preparation. This configuration lowers the danger of contamination of the laboratory atmosphere during the preparation procedure.

4. Optical properties

The chalcogenide glasses belong to solids having the forbidden band $E_g > 2$ eV and, therefore, they can transmit the radiation in near, middle and far infrared spectra in opposition to SiO_2 glass which is transparent up 2.1 µm (Table 1).

Table 1. Some physical properties of selected special glasses.

Glass	Phonon energy (cm^{-1})	Transmission range (µm)	Refraction index (n)
As_2S_3	350	0.5 - 6	2.35
As_2Se_3	360	0.8 - 10	2.70
$Ge_{25}Ga_{10}S_{65}$	380	0.6 - 7	2.55
$Ge_{25}Ga_5As_5S_{65}$	330	0.6 - 7	2.58
Fluoride Glass	440 - 650	0.25 – 6.5	1.52
Heavy Metal Oxide Glass	590 - 850	0.4 - 7	2.65
SiO_2	1150	0.25 - 2	1.148

The transparency range of these glasses depends on the composition and is situated in the range from 0.5 µm to 7 µm for glasses on the base of sulphides, from 0.8 to 12µm for selenide and 1.2 to 16 µm for telluride glasses.

Refraction indices (n) and the values of transparencies (%) also depend on glass composition as can be seen in Table 1.

The region of the transparency is limited by an intrinsic absorption at short and long wavelengths, the position at short wavelength corresponds to $\lambda = h.c/E_g$, where λ is wavelength, h - Plank constant, c - light velocity and E_g is energy width of the forbidden band. Long - wave cut-off is caused by the vibrations of molecular bonds in solids. The survey of the values of transmission interval, and refraction index for some sulphide, selenide and telluride glasses is given in Table 1.

5. Extrinsic absorption

In the transparency range (from short to long wavelength cut off) it can be observed absorption bands caused by impurities, which are called extrinsic absorption. Extrinsic absorption determines the intensity of absorption bands of impurities built up in the glass network, for well determined wavelengths. The concentration of impurities can be estimated from the intensity of extrinsic absorption bands [15]. The extrinsic absorption in chalcogenide glasses can be caused by two kinds of impurities:

- oxide impurities - the presence of O -X bonds
- hydride impurities - the presence of H - X bonds

The survey of the extrinsic absorption of selected oxide and hydride impurities is given in Table 2 and 3.

Table 2. The extrinsic absorption bands of selected oxides.

Compounds	Bonds	Wavelengths (µm)
As_2O_3	As - O	7.90s, 9.50w, 12.34vs
Sb_2O_3	Sb - O	13.55m, 14.53s, 17.60s
SiO_2	Si - O	9.27vs, 12.50m
GeO_2	Ge - O	10.40m, 10.77s, 11.40vs
GeO	Ge - O	12.40vs, 18.18m
SeO_2	Se - O	10.67w, 11.06vs, 13.96s
TeO_2	Te - O	12.95s , 15.50vs

Intensity of absorption bands: vs - very strong, s - strong, m - middle, w – weak, sh – absorption shoulder

Table 3. The survey of absorption bands of some hydride impurities.

Impurities	Wavelength (µm)
O - H	6.3s, 2.93vs, 2.78m, 2.24m, 1.45w
S - H	4.01s, 3.70m, 3.11m, 2.54w,2.05w
Se - H	4.57s, 4.12m, 3.53w, 2.32w
Te - C	5.07m
C - H	3.5m, 3.41m

Intensity of absorption bands: vs -very strong, s - strong, m - middle, w - weak, vw - very weak

6. Electrical properties

Chalcogenide glasses belong to the group of semiconductor materials and the mechanism of electrical conductivity is quite different from the oxide glasses. Most oxide glasses show an ion electrical conductivity opposite to chalcogenide glasses that exhibit electron conductivity. The values of electrical conductivity depend on the chemical composition and on the forbidden gap, E_g. For example, the value of d.c. electrical conductivity in a telluride based glass is about $10^{-1}\,\Omega^{-1}cm^{-1}$. The highest value was found in glassy Se: ~ $10^{17}\Omega^{-1}cm^{-1}$.

The most important electrical properties are: d.c. conductivity, a.c. conductivity and switching effects: threshold and memory effects.

Table 4. The luminescence peaks in $Ge_{25}\,Ga_{10-x}\,S_{65}\,Pr_x$.

Concentration X (wt.ppm)	Wavelengths and intensity of luminescence			
	λ (μm)	I (a.u.)	λ (μm)	I (a.u.)
500	1.339	1.32		
1000	1.339	7.90	1.534	0.80
3000	1.340	4.65	1.607	0.10
6000	1.341	3.70	1.601	0.07
12000	1.341	3.90	1.611	0.30

The changes in electrical and dielectric parameters finely reflect the structural changes in chalcogenide glasses and help to determine the influence of various technological parameters, impurities and doping elements. The relaxation mechanism of the glass structure is not fully understood, although the data of both electrical and dielectric properties are known. The presence of structural disorder, inhomogeneities, as well as the glass temporal and temperature stability can be found from the temperature dependency of d.c. conductivity as well as from both temperature and frequency dependencies of complex permittivity. Therefore, it can be said that the chemical and physical quality of chalcogenide glasses can be characterised from above discussed measurements.

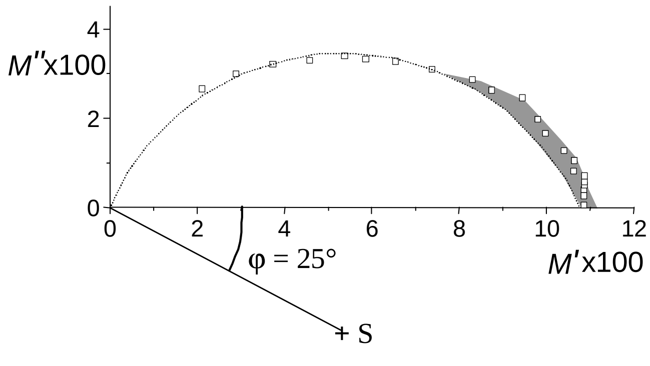


Fig. 4. Low-temperature PL spectra of $Ge_{0.25}Ga_{0.1-x}S_{0.65}Er_x$ are shown. Full and dashed lines correspond to temperatures of 5 and 120 K, respectively.

From the measurements of direct current conductivity only one mechanism of conductivity was evidenced (values of activation energy: 0.8 - 0.95 eV). The complex permittivity is important for characterising the glass. It is advantageous to analyse the measured temperature and frequency dependencies by means of complex electrical modulus (the measurement of the temperature and frequency dependencies of complex electrical modulus). For illustration, it is shown the dependence of electrical complex modulus M'' versus M' (Fig. 4) and the dependencies of complex electrical modulus

(M'' versus f) respectively) measured at different temperatures (215, 243, 270 ^{o}C for $Ge_{25}Ga_{10-x}Pr_xS_{65}$ glasses with x =1000 wt.ppm (Fig. 5). Similar results were obtained for As-Se-Te, As_2Se_3; GeSeTe doped with Er, and Pr ions, and concentration of 1000 wt.ppm.

Methods for the measurements of frequency dependent conductivity modulus are very suitable to investigate sulphide, selenide, and other chalcogenide glasses for optimization of the technological procedures and chemical composition. The influence of the synthesis parameters on the microstructure and short range order of As_2S_3 glass, and, therefore, on its physical properties was discussed by Luksha, Borkach and Ivanitsky [16].

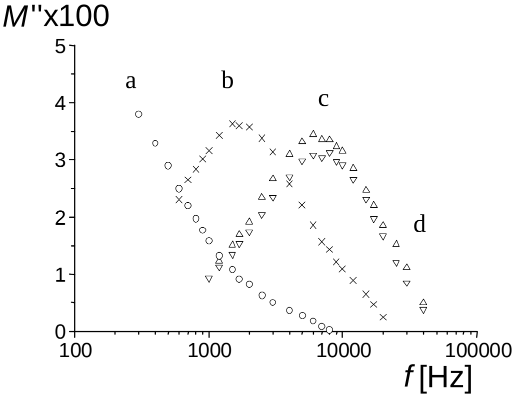


Fig. 5. Photoluminescence spectra measured at four temperatures (a) 5 K, (b) 100 K, (c) 150 K and (d) 200 K, for the sample As_2S_2Se doped with Er.

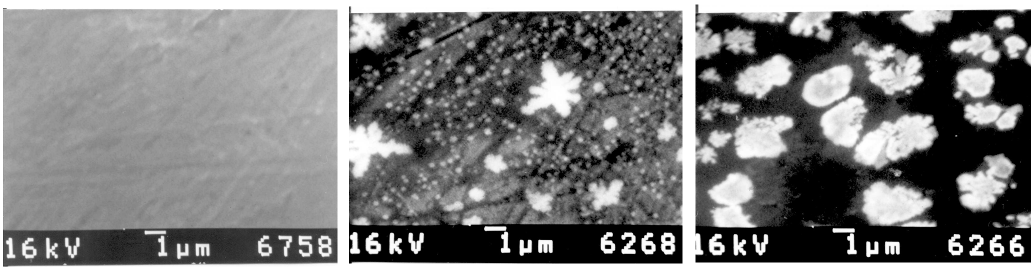
7. Active chalcogenide glasses

7.1 Survey

The chalcogenide glasses based on sulphides and, selenides are very promising materials for various photonic applications. For a long time these glasses have been studied for passive devices and optical fibers for transmission of infrared radiation. These glasses are also attractive for active devices due to their low phonon energies, higher values of the refractive index, and their transparency in middle infrared spectrum. These characteristics are better than in silicate and ZBLAN glasses. For example, Pr^{3+} doped silica glasses provide a total radiation quantum efficiency of about 3 – 4 %. For sulphide glasses the efficiencies of up to 60 % are predicated. In this paper the following glassy systems were investigated: As-S, As-Se, Ge-Ga-S, Ge-Ga-As-S, undoped and doped with various rare earth ions (RE^{3+}). The main problem is the preparation of these glasses with high chemical and physical purity, low OH group concentration (below 10^{-4} mol%) and low physical defects and clusters. The glasses were investigated by a set of physical measurements including chemical and X-ray analysis, scanning and electron microscopy, infrared absorption spectra, photoluminescence, permittivity and d.c. conductivity. The optimum RE concentration in homogeneous and cluster free glasses is situated in the range 500 – 1500 wt.ppm. The highest values of the photoluminescence were observed on Ge-Ga-As-S glasses doped with Pr^{3+} ions. At higher RE and OH concentration the development of clusters into host glasses was observed.

The rapid development of the telecommunication networks requires the integration of various optoelectronic devices such as multiplexers, modulators and optical amplifiers. In this respect, rare earth doped fibers are key components for active systems, and most of them are made from silica. In some cases the limitations of silica stimulate the search for new materials. This is the case when a low phonon energy is required for optimum quantum efficiency. The requirements for host materials may be summarized as follows:

1) Low transmission losses both at excitation and emission wavelengths.
2) Convenient rare earth solubility .
3) Significant lifetime of active level.



a b c

Fig. 6. Development of clusters when the OH group concentration increases: a → c.

There is a growing interest in new families of special glasses involving fluoride, chalcogenide and heavy metal oxide glasses, which extends the research and application due to their outstanding properties in opposition to the case of SiO_2. These glasses and related optical fibres can be used as passive fibres in power delivery systems [Er: YAG - 2.97µm, CO - 5.3 µm, CO_2 -10.6 µm] and, due to other suitable properties, as lower phonon energies, and higher refraction indices they can be used as active optical fibres. Chalcogenide glasses suitable for drawing active fibers are prepared by doping the host glasses with ions of rare earth elements as e.g. Pr, Er, Ho, Dy, Nd, etc.

Chalcogenide glasses on the base of sulphides, selenides, selenide – tellurides, binary or multicomponent alloys are promising materials for applications in optoelectronics. Hopefully, OH concentration should be less than 5×10^{-5} mol %. In addition, scattering arisen from inhomogeneities and physical defects must be small enough to keep the background losses below 1 dB/m [12]. The attention in this paper is focused on As-S, As -Se, As-S-Se, As-Se-Te, Ge-Se-Te systems. As already noted, the main problem consists in the preparation of these glasses in high chemical and physical purity because even low amount of impurities very strongly influences the solubility of RE^{+3} ions in the host glass, optical and fluorescence properties and the growth of clusters.

7.2 Characterisation and properties

The difference in the batch composition and that of the prepared glass was less than 6% on average. The concentration of OH groups was calculated from the intensity of the absorption band at 2.93 µm and is situated between 10^{-4} mol% and 10^{-5} mol%.

The survey of present extrinsic absorption bands is given in Table 1 (OH - 2.93 µm, SH - 4.01µm, SeH - 4.57 µm, H_2O - 6.33µm, intrinsic band of Pr - ~ 2 µm). From this table results that the transmission of glasses decreases with the increase of Te concentration due to the increased values of the refraction index. For some glasses with higher Te concentration the transmission decreases due, also, to partial crystallisation and phase separation. In these cases the scattering losses increase.

X-ray analysis revealed the presence of crystalline phases in several selenide-telluride glasses with high Te concentration. Undoped and doped samples were studied by electron microscopy. The results can be summarised as follows:

- The pure undoped sulphide and selenide glasses are homogenous, without crystalline particles, clusters and chemical inhomogeneities (Fig. 1).
- The homogeneity of RE doped sulphide, selenide, selenide - telluride glasses (Pr, Er) depends on the kind of RE^{3+} ions and their concentration and chemical forms in which were added (sulphides, oxides, chlorides, separate elements).
- The phase separation and the growth of clusters depend on the concentration of RE ions and OH groups. Generally speaking, when the concentration increases, an increase of cluster size is observed.
- Selenide - telluride glasses show less thermal stability and at higher tellurium concentration is observed a phase separation (Fig. 2).

- The optimum RE concentration, for which the prepared sulphide and selenide are homogeneous and cluster free, seems to be between 500 and 1500 wt.ppm.

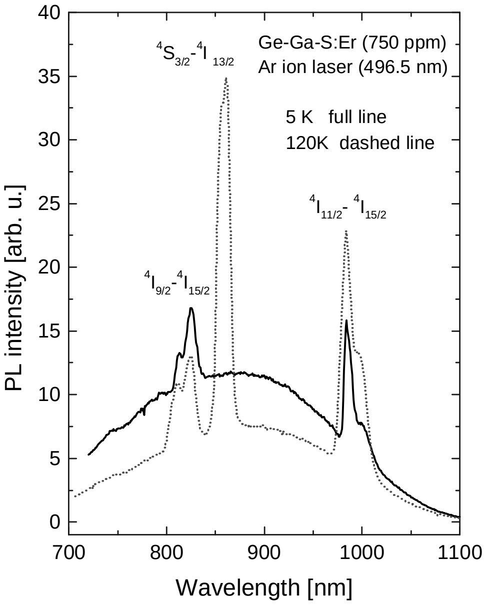


Fig. 7. Photoluminescence spectrum of Ge-Ga-S glass doped by Er measured at the temperatures of 5 K and 120 K.

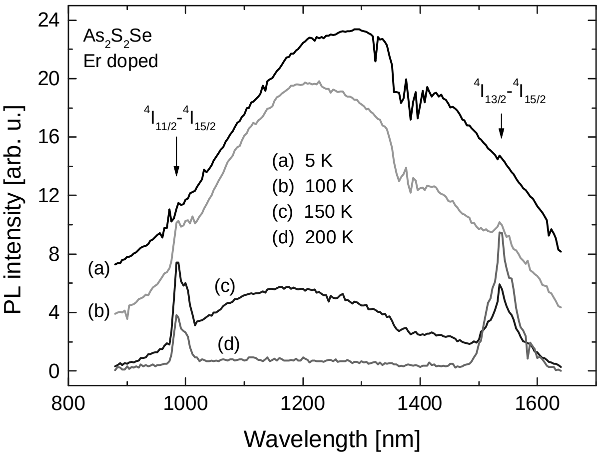


Fig. 8. Photoluminescence spectra of Er doped As_2S_2Se glass at various temperatures.

The photoluminescence (PL) appears as a sensitive tool for monitoring the formation of RE related clusters. The temperature dependence of PL spectra revealed different behaviour in $Ge_{0.25}Ga_{0.1}S_{0.65}$ ($Ge_{0.25}Ga_{0..05}As_{0.05}S_{0.65}$) and As_2S_2Se (As_2S_3, As_2Se_3) systems. Typical PL spectra for $Ge_{0.25}$ $Ga_{0.1}S_{0.65}$ and As_2S_2Se glass compositions doped with Er are shown in Figs. 7 and 8, respectively. PL spectra of Ge-Ga-S: Er (750 ppm of Er) are shown in Fig. 7 for two temperatures. We can see that crystalline Er phase is present at this level of doping, as demonstrated by two sharp transitions $^4I_{9/2} \rightarrow {}^4I_{15/2}$ and $^4I_{11/2} \rightarrow {}^4I_{15/2}$. Beginning with 15 K another peak assigned to $^2G_{9/2} \rightarrow {}^4F_{9/2}$ does appear, its intensity is steadily growing and dominates the spectrum at 120 K. In our experiments we used Ar ion laser for excitation and, therefore, the energy levels of Er^{3+} ion up to the $^4G_{11/2}$ level could be excited. We believe that the temperature induced phonon-assisted upward transitions ($^4G_{11/2} \rightarrow ^2G_{9/2}$) take place and they are responsible for the observed temperature dependence of PL spectra. Further experiments with various power and wavelength of the excitation are needed to verify this hypothesis.

A temperature dependence of PL spectra for As_2S_2Se: Er system is shown in Fig. 8. The luminescence of the base glass is considerably narrowed with decreasing temperature and shifts towards low energies. Radiative transitions via deep laying level dominate low temperature spectra of As_2S_2Se system and shield the observation of RE related transitions. The emission appears as a wide band at roughly half the optical band gap. Kolomiets and his co-workers have shown long-time ago that the luminescence spectra obtained in crystalline As_2Se_3 and As_2S_3 are very similar to those in the corresponding glasses, and they infer that the same deep recombination centres are present in both amorphous and crystalline forms.

Table 5a. Average values of mechanical properties of special glasses.

Material	Fracture strength (MPa)	Hardness (kgf.mm^{-2})	Thermal expansion (10^{-7}/°C)	Fracture toughness (MPa.m$^{1/2}$)
Fluoride	20	225 - 250	150 - 180	0.25 – 0.27
Chalcogenide	20	100 - 200	240 – 250	0.20
HMO	25	600	120 – 180	0.35 – 0.45
Silica	70	800	5.5	0.70 – 0.80

Table 5b. Comparative merits of infrared fibres.

Material	Attenuation	Flexibility	Fabrication rate	Environmental stability	Ageing
Fluoride	very good	good	good	medium	good /medium
Chalcogenide	medium	good	good	medium	good/medium
HMO	medium	poor	medium	good	good
Hollow	good	good	good	good	good

Low temperature spectroscopy was used to obtain information on the optimal RE^{3+} concentration at which doped glasses are homogeneous and cluster free. The results of luminescence measurements of $Ge_{25}\, Ga_{10-x}\, S_{65}\, Pr_x$ glasses are given in Table 4. From this table the maximum value of the luminescence intensity was found for x situated in the range 1000 - 3000 wt.ppm. At higher concentration of Pr^{3+} the value of the intensity decreases due to clustering. Generally, it can be concluded that quantum efficiency of the luminescence is highest in sulphide glasses (about 80 %), and it is lower in fluoride and HMO glasses (about 20 %). For comparison, SiO_2 displays only 3 – 4 % quantum efficiency [13, 15].

The homogeneity of the glasses containing RE^{3+} (Pr, Er, Nd, Ho, Dy, etc.) depends on the nature of the RE^{3+}, their concentration, doping precursor compounds and OH group concentration. The dependence of the growth of the clusters on OH group concentration is shown in Fig. 6, which confirms that with increasing OH group concentration the clusters are observed in host glasses in higher concentration and larger size [13, 15].

The measurements of temperature dependencies of direct conductivity, temperature and frequency permittivity (modular spectroscopy) enable the physicist to determine the structural changes due to various RE^{3+} and OH group concentration and due to other physical defects.

8. Applications of passive and active special glasses in optical fibers

The survey of some applications for passive and active glasses and fibers is given below. Recent developments are discussed in [16-27].

8.1 Passive Applications

Laser power delivery system

- Er: YAG laser (2.97 μm) As-S, Ge-Ga-S, fluoride, sapphire etc
- CO laser (5.3 μm) As-S , As-Se , Ge-As-S, sapphire
- CO_2 laser (10 μm) As –Se, As-Se-Te, Ge-Se-Te
- Transmission in the atmospheric (2 – 5 μm) region of the spectrum
- Medical Free Electron Laser (2 – 10 μm)
- Anti – reflection (AR) coating

Chemical Sensing

- Aqueous, non – aqueous, toxic chemicals
- Polymers, paints, pharmaceuticals
- Condition Based Maintenance (CBM)
- Cone Penetrometer System
- Active Coatings
- Bio – medical applications

Thermal Imaging & Hyperspectral Imaging

- Coherent fibre bundles

Near Field Microscopy

- Imaging and spectroscopy

8.2 Active applications

Rare Earth Doped Fibers

- Fibers Laser and amplifiers - 1.08 μm (Nd), 1.34 μm (Pr), 1.34 μm (Dy)
- Infrared Scene Simulation (IRSS), emission in the regions: 2 – 5 μm and 8 –11 μm.

Chemical Sensing

- toluene detection: 3.42 μm (Pr^{3+}) and 3.62 μm (Er^{3+})
- CO_2 detection: 4.27 μm (Dy^{3+})

Non linear optics

- Optical switching
- Second Harmonic Generation
- Frequency mixing
- Electrical poling

9. Conclusions

Several general conclusions can be drawn.

Most of special glasses can be used in applications in infrared optics and optoelectronics.

The glasses can be used for the preparation of optical fibers both for passive and active applications.

The glasses are stable, but some fluoride and HMO glasses have the tendency to the crystallisation and are hygroscopic.

For preparation of highly pure glasses with diminished OH, oxide and low physical defect concentrations, new methods were developed. The purification methods were based on the preparation in a reactive atmosphere. In this way, the average concentration of hydride impurities was lowered below 5×10^{-5} mol.

HMO glasses are more difficult to be prepared with a high purity. The OH group concentration is about 1 – 2 orders higher than in fluoride glasses. This is the reason why the treatment in reactive atmosphere is less effective.

Optical losses of fluoride optical fibers are about 1 dB/km (the theoretical value is 10^{-2} dB/km); optical losses of chalcogenide and HMO fibers are many times higher (0.1 – 1 dB/m), but the glasses are good for photonics applications on short distance.

Rare earth ions are introduced into the base glasses in concentrations from 500 to 6000 wt.ppm; homogeneous samples containing up to 3000 wt.ppm of Pr^{3+} in sulphides glasses were prepared.

High RE and OH group concentration favours the growth of clusters.

Sulphide glasses exhibit quantum efficiency of fluorescence of about 80%, while for fluoride and HMO glasses the efficiency is about 15 – 22%.

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