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CHALCOGENIDE GLASSES FOR OPTICAL AND PHOTONICS APPLICATIONS

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A short review of relevant parameters, such as phonon energy, transmission range and refraction index, that distinguish previously and presently studied chalcogenide glasses from silica based ones is given. Chalcogenide glass systems GeSe, GeSeTe and As_2Se_3 have been prepared and characterized by absorption spectroscopy and low-temperature photoluminescence. Both absorption and low-temperature photoluminescence spectra reveal shifts of absorption edge and/or luminescence band to longer wavelength due to Te → Se substitution. Luminescence band shows little change with increasing temperature up to 200 K and considerable shift to shorter wavelength appears when room temperature is approached. No influence of Te → Se substitution on the position or spectral shape of luminescence band is observed at room temperature.

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1. Introduction

In recent years the research has been focused on the preparation of special glasses, i.e. fluoride, chalcogenide and heavy metal oxide ones that can transmit optical radiation above 2 μm and also other optical parameters exceed those of silica based glasses. The attention in this paper is focused on chalcogenide glasses, on preparation of high quality base glass, doping by RE elements and characterization of optical properties.

Chalcogenide glasses always contain one or more chalcogen element, sulphur, selenium or tellurium in combination with elements from IVth, Vth or VIth group of the periodic system of elements. Glasses are solids with covalent bonds, maximum of ionic conductivity is 9% and their properties are significantly different from oxide glasses on the base of SiO_2. Chalcogenide glasses based on sulfide, selenide and telluride alloys in binary or multi-component systems are very promising materials for various optical and photonic applications in the spectral range 0.6 to 15 μm. These glasses are being studied mostly for applications as passive devices (lenses, windows, fibres) but these glasses are also attractive for preparation of active devices such as laser fibre amplifiers and non-linear components. For this purpose the glasses are doped with ions of rare-earth elements (RE). One of the main problems connected with RE doping lies in the preparation of glasses with high chemical and physical purity. Therefore new methods of purification and preparation had to be developed to decrease concentration of hydride and oxide groups (OH, SH, SeH, H_2O, As_2O_3, GeO_2 etc.) below $10^{-4} – 10^{-5}$ mol% and concentration of physical defects below 10^3 cm^{-3} [1]. The values of optical losses about 1 dB/m could only be achieved when the above mentioned requirements on chemical and physical purity of base glasses are met. At present the attention is paid to the study of glass materials suitable for infrared optical fibres for laser power delivery (Er:YAG, CO and CO_2 lasers), active laser fibres and non-linear optical elements.

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In this paper we report the preparation of As_2Se_3, Ge-Se and Ge-Se-Te glass systems and the investigation of their optical properties. These glasses possess a promising potential for laser power delivery in NIR and IR regions of the spectrum. Due to the heating of optical fibres a good temperature stability of corresponding glass material is required. The optical transmission in the range 2.5 to 12 μm, including Er:YAG and CO_2 lasers, is largely determined by the presence of oxide and hydride impurities. Thus the removal of OH groups is essential.

2. Experimental

2.1 Preparation

Glasses were prepared by direct synthesis from pure starting elements. Chalcogenide glasses belong to substances which have an incongruent melting point, exhibit a high partial vapour pressure during melting and therefore the synthesis must be carried out in sealed evacuated quartz ampoule. The synthesis conditions are widely varied - they depend on the glass composition, glass forming region and glass forming ability.

The major sources of hydride, oxide and carbon related impurities seem to be starting elements (As, Ge, S, Se, Te) [2,3] and therefore re-purification of these elements must be carried out. This purification of starting elements has always been performed with the exception of two samples discussed in connection with transmission spectra. The sublimation under vacuum and the reactive atmosphere proved to be very effective for S, Se, As and melting under vacuum showed similar effects for Ge. The purification and preparation must be done in many steps before and during the synthesis. The technological procedures involving the distillation, synthesis of undoped and RE doped glasses and the preparation of preforms for fibres drawing were carried out in one special quartz ampoule [3]. For the removal of oxide impurities a gettering was used by exploiting aluminium (Al) in the amount of 100 wt. ppm as the gettering agent. This procedure lowers the possibility of contamination during preparation steps. The melting temperature of glasses depends on their composition; for glasses containing As it is about 700 - 800 °C, for Ge about 850 - 950 °C. The melting time was 15 - 20 hours and then the ampoule with glass melt was cooled to room temperature. A more detailed information on this novel purification and preparation method is given in [3,4]. Preforms of 10 mm in a diameter and 50 – 80 mm in length were obtained. Similar method could be applied to prepare glasses doped with RE elements for preparation of active optical fibres. The following RE elements Pr, Er, Nd, Dy and Ho have been used in our laboratory by using various precursors.

Prepared glasses have been examined by various diagnostic measurements –absorption spectroscopy, light scattering, elemental X - ray micro-analysis, scanning electron microscopy (SEM) and photo-luminescence (PL) spectroscopy and measurements of direct electrical conductivity (dc). Transmission spectra in the visible range have been measured by Specord M400 and in NIR by Matson Galaxy 3000. Photoluminescence (PL) spectra were taken at various temperatures and various levels of excitation by He-Ne and Ar ion lasers in an optical He closed cycle cryostat enabling measurements in the range 3.5 – 300 K. The 1m focal length monochromator with the cooled EI Ge detector or cooled GaAs photo-multiplier enables sensitive and high resolution measurement in the spectral range 400-1800 nm by using the lock-in technique and the computer controlled data collection. Dc electrical conductivity has been measured by vibrational electrometer.

3. Results

3.1 Optical properties, absorption spectroscopy

Some relevant parameters that distinguish reviewed chalcogenide glasses from silica based ones, such as phonon energy, transmission range and refraction index, are given in Table 1 for selected glasses [3].

Table 1. Some physical properties of selected chalcogenide glasses.

Glass	Phonon energy (cm^{-1})	Transmission range (μm)	Refraction index
As_2S_3	350	0.5-6	2.35
As_2Se_3	360	0.8-12	2.7
As_2Te_3	380	1.5-15	3.5
$Ge_{20}Se_{80}$	360	0.9-12	2.35
$Ge_{25}Ga_{10}S_{65}$	380	0.6-7	2.58
$Ge_{25}Ga_5As_5S_{65}$	330	0.6-7	2.58

The region of transparency is limited by an intrinsic absorption at short and long wavelengths. Within the transparency range, limited by short and long wavelength cut offs, could be observed various absorption bands caused by chemical impurities or complexes that are called extrinsic absorption. The concentration of these impurities could be calculated from the intensities of observed bands. Most of extrinsic absorption could be assigned to oxide and hydride compounds. The survey of typical extrinsic absorption centres, positions and intensities of absorption peaks are given in Table 2.

Table 2. The survey of extrinsic absorption bands.

Compound	Bond	Position [nm] and intensity
As_2O_3	As-O	7.90 s, 9.50 w, 12.34 vs
GeO_2	Ge-O	10.40 m, 10.77 s, 11.40 vs
SiO_2	Si-O	9.27 vs, 12.50 m
SeO_2	Se-O	10.06 vs, 13.96 s
H_2S	H-S	4.01 s, 3.70 m, 2.54 w
H_2Se	H-Se	4.57 s, 4.12 m, 3.53 w
OH group	O-H	2.93 vs, 2.78 m, 2.24 m
Carbonate	C-H	3.50 m, 3.41 m
H_2O	O-H	6.30 s

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

The discussed glasses are also attractive for preparation of active devices due to their low phonon energies, higher values of refractive index and their transparency in middle infrared range. In the course of our study the following glass systems As-S, As-Se, Ge-Ga-S and Ge-Ga-As-S doped with various RE^{3+} ions (Pr, Er, Ho, Nd and Dy) have been investigated.

3.2 Photoluminescence spectroscopy

Photoluminescence (PL) spectra of $Ge_{20}Se_{80}$ and multi-component alloys $Ge_{20}Se_{80-x}Te_x$ with various amounts of Te have been measured at different temperatures. The influence of substitution of Te for Se is demonstrated in Fig. 1, where low temperature PL spectra of $Ge_{20}Se_{80}$ and $Ge_{20}Se_{80-x}Te_x$ with x = 5, 8 and 10 are shown. A shift of dominant luminescence band from 1150 nm ($Ge_{20}Se_{80}$) to 1550 nm ($Ge_{20}Se_{70}Te_{10}$) could be seen. A modest shift of luminescence band to longer wavelength with increasing amount of Te could be seen. The structure at about 1350 nm is due to absorption of emitted luminescence radiation on water vapours in the air. It is seen because there is a strong signal within the water vapours absorption range. Both position and line width of the luminescence band are not strongly temperature dependent up to 200 K but considerable change appears when room temperature is approached. Finally, at room temperature both $Ge_{20}Se_{80}$ and $Ge_{20}Se_{80-x}Te_x$ glass systems exhibit a broad luminescence at the same wavelength range around 900 nm. No spectral difference due to Te → Se substitution is observed at room temperature. From detailed inspection of measured temperature dependences we come to the suggestion that actually the luminescence band that dominates at low temperature is quenched at about 250 K and new luminescence channel takes over and dominates the spectra at 300 K. Both the position and the spectral shape of this room temperature PL band do not show any dependence on Te → Se substitution.

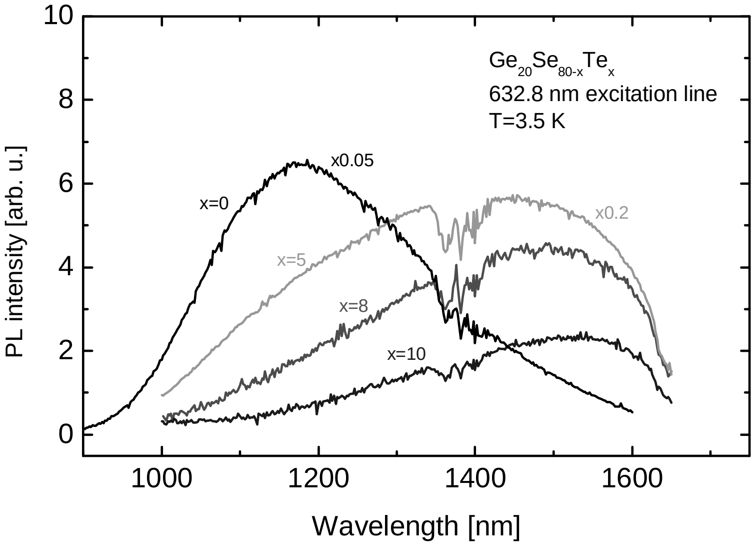

Fig. 1. Low temperature PL spectra of $Ge_{20}Se_{80-x}Te_x$ are shown for x = 0, 5, 8 and 10. The substitution of Te for Se significantly shifts the luminescence band to longer wavelengths. A modest shift to longer wavelength with increasing Te content is demonstrated.

Photoluminescence (PL) appears as a sensitive tool for monitoring the formation of RE related clusters. Typical low temperature FL spectra of As_2Se_3/Er is shown in Fig. 2.

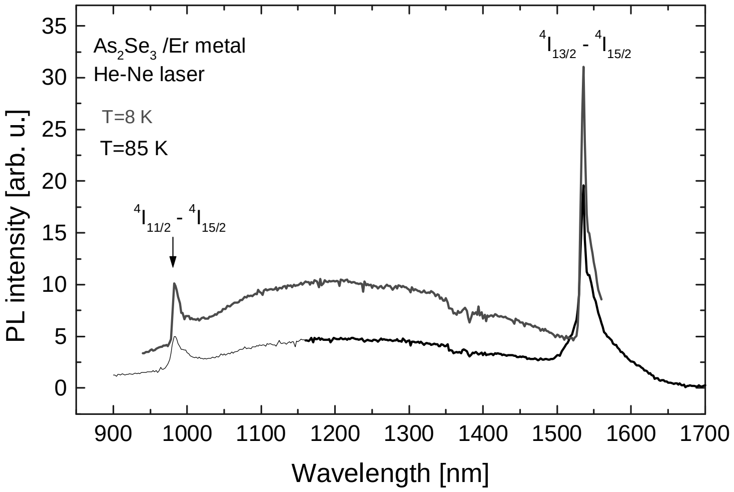

Fig. 2. Low temperature PL spectra are shown at 8 and 85 K. Beside the broad band mediated by deep levels in the base glass we can also see characteristic narrow 4f-4f transitions of Er^{3+} ion at 977 and 1538 nm.

Radiative transitions via deep laying levels dominate low temperature spectra of As_2Se_3 base glass system. The emission appears as a wide band at roughly half the optical band gap [5]. For GeSeTe glass systems the broad PL band of the base glass is shifted to 1500 nm.

4. Conclusions

The results and conclusions could be summarised as follows:

- The developed method of chalcogenide glass synthesis and purification appears to be very effective, the average concentration of hydride and oxide impurity concentrations was kept below 5×10^{-5} mo%., and concentration of physical defects below 10^3 cm^{-3}.
- Prepared glasses are homogeneous without crystalline particles, clusters, chemical inhomogeneities and physical defects. Concentration of hydride and oxide impurities calculated from intensities of corresponding absorption bands is about $5 \times 10^{-4} – 10^{-5}$ mol%.
- Homogeneity of chalcogenide glasses doped with RE ions depends on the kind of RE and their concentration. The optimum RE concentration seems to be 500 – 1500 wt ppm. The rise of clusters and the phase separation depends considerably on OH group and RE^{3+} concentrations. When these concentrations exceed certain limits (10^{-4} mol% and 2000 wt ppm, respectively), the rise of clusters and phase separation could be observed.
- The role of multi-phonon transitions has been demonstrated by measuring the temperature dependence of PL spectra of RE doped glass systems. This is also supported by different behaviour of inner shell transitions, as a function of temperature, in different glasses. Multi-phonon transitions are particularly important in the case of high energy excitation (He-Ne, Ar ion lasers).
- Both short and long wavelength absorption edges shift towards longer wavelength as a result of Te $\rightarrow$ Se substitution in $Ge_{20}Se_{80-x}Te_x$ glass system. This effect is more pronounced at the short wavelength absorption edge. At low temperature there is a distinct shift of PL band towards longer wavelength due to Te $\rightarrow$ Se substitution. Little change of PL spectra with increasing temperature has been observed in the temperature range 3.5 – 200 K. However, above 200 K the PL band that dominates the spectra at low temperature starts to quench and a new band around 900 nm appears. The luminescence band at 900 nm dominates the spectra at 300 K in all measured samples and no spectral dependence on Te $\rightarrow$ Se substitution is observed at this temperature. This “shift” of PL band to shorter wavelength, when going from 200 to 300 K, exhibits opposite temperature dependence than that of the band gap. This fact supports our suggestion that new luminescence mechanism opens above 200 K.
- Most of chalcogenide glasses could be used in infrared optics and optoelectronics as passive or active fibres and various other components. Main applications are: laser power delivery systems for Er:YAG, CO and CO_2 lasers, anti-reflection coating, chemical sensing, thermal imaging, fibre lasers and amplifiers, non-linear optics.

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