

SULPHIDE GLASSES DOPED WITH RARE EARTH ELEMENTS

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Sulphide glasses of GeGaS and GeGaAsS systems doped with rare earth ions are promising materials for various photonic applications. Because the solubility of rare earth elements is influenced by the purity of host glass, namely by OH group concentration, the attention has been paid to the preparation of highly pure and homogeneous undoped and rare earth doped glasses. Particularly the systems $Ge_{0.25}Ga_{0.1-x}S_{0.65}Pr_x$ and $Ge_{0.25}Ga_{0.05-x}As_{0.05}S_{0.65}Pr_x$ with $x = 0.05, 0.1, 0.3$ and 0.6 wt.% have been prepared. Synthesised material systems have been characterised by chemical and X-ray analysis, scanning electron microscopy, light scattering, Raman and low-temperature photoluminescence spectroscopies. The optimal Pr concentration has been found to be around 0.1 wt.%. For higher Pr and OH group concentrations the constitution of clusters has been observed.

Keywords: Sulphide glasses, Optical fibers, Fluorescence, Luminescence

INTRODUCTION

Active devices based on the spectroscopic properties of rare earth (RE) cations are the subject of numerous studies for potential applications in the field of optoelectronics. Of particular interest are optical amplifiers for telecommunications and fiber lasers. Also active planar waveguides make an attractive option for integrated optics.

First developments have been tested on classical materials such as silica fibers [1]. Erbium doped fibre amplifiers (EDFA) are a typical example. However in some cases, the material limitations are excessive, resulting in problems which cannot be overcome. The requirements for host materials may be summarized as follows:

1. Transmission losses must be low enough both at excitation (pumping) and emission wavelengths.
2. Rare earth solubility must be large enough.
3. The lifetime of the active level must be long enough.

This last requirement relates to extrinsic and intrinsic factors. Extrinsic factors include impurity quenching and physical defects. Intrinsic factors encompass phonon assisted de-excitation and concentration

quenching. When the energy separation between excited level and lower level is large by comparison to the host phonon energy, the phonon assisted de-excitation rate is small and radiative transfer becomes predominant.

Thus since silica phonon energy is too large for a selected transitions, glasses with lower phonon energies are required. Fluoride glasses make a first possible option which has been largely investigated. This is not always sufficient, and chalcogenide glasses make the next choice among vitreous materials [2 - 4]. Sulphide glasses such as As_2S_3 and GeS_{2+x} are stable glasses which may be obtained as large and homogenous samples and have been successfully drawn into fibres. However rare earth cations are difficult to incorporate into these glasses, probably for structural reasons. From systematic attempts, we have observed that lanthanide solubility was enhanced when gallium was included in the basic glass composition. This paper reports some results on the incorporation of rare earth elements into germanium sulphide glasses. Two compositions were selected: $Ge_{0.25}Ga_{0.1}S_{0.65}$ and $Ge_{0.25}Ga_{0.05}As_{0.05}S_{0.65}$. Arsenic was included as a stabilising agent.

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EXPERIMENTAL PROCEDURES

Several sets of samples have been synthesised. A first group concerns praseodymium-doped glasses with dopant concentrations ranging from 0.05 - 0.6 wt.%. Various precursors - Pr_2S_3 , Pr_2O_3 , PrCl_3 and Pr metal - have been used in two glass hosts: Ge - Ga - S and Ge - Ga - As - S. Undoped and doped $\text{Ge}_{0.25}\text{Ga}_{0.1-x}\text{S}_{0.65}\text{Pr}_x$ and $\text{Ge}_{0.25}\text{Ga}_{0.05-x}\text{As}_{0.05}\text{S}_{0.65}\text{Pr}_x$ glass samples with x ranging from 0 to 0.6 wt.% have been prepared. The details of the technology have been described elsewhere [5]. We briefly describe facilities used for spectroscopic characterisation. Photoluminescence (PL) spectra have been measured at various temperatures and levels of excitation power. The experimental set-up consists of the optical cryostat based on Helium Refrigerator System (Balzers, USA) and automatic temperature controller that enables to measure at any temperature in the range 4 - 300 K. PL spectra are analysed by 1m focal length monochromator (Yobin-Yvon, THR 1000) coupled with N_2 -cooled Ge detector and/or N_2 -cooled S1 photomultiplier, using lock-in technique and computer controlled data collection. He-Ne and Ar ion lasers have been used for excitation. The excitation power densities have been varied in the range 0.1-100 mW/cm² using suitable neutral density filters. Bruker IF S55, 180 degree fourier spectrometer, together with Nd:YAG laser (4 - 15 mW) has been used for Raman spectroscopy.

RESULTS

Prepared glasses are yellow-orange or red (with arsenic) colored, and they also exhibit the characteristic absorption bands of RE cations. No visible defects or crystalline phase are seen under microscope, and no absorption peak appears in X-ray diffraction patterns. Current samples are small cylinders, 1 cm in diameter and a few centimetres in length.

A set of measurements including chemical and X-ray analysis, light scattering, scanning electron microscopy (SEM), infrared absorption, Raman and photoluminescence spectroscopies have been carried out on prepared samples. The results obtained by SEM could be summarised as follows:

- Base glasses $\text{Ge}_{0.25}\text{Ga}_{0.1}\text{S}_{0.65}$ and $\text{Ge}_{0.25}\text{Ga}_{0.05}\text{As}_{0.05}\text{S}_{0.65}$ appear homogeneous and free of crystalline inclusions
- The homogeneity of the samples containing RE ions (Pr, Er, Dy, Nd, Ho and Sm) varies according to the nature of the RE and the chemical precursor (sulphide, oxide, chloride, elemental RE). RE concentration is also an important parameter.

Typical observations on $\text{Ge}_{0.25}\text{Ga}_{0.1-x}\text{S}_{0.65}\text{Pr}_x$ samples are shown in figure 1 for various Pr^{3+} and OH group concentrations. Pr_2S_3 precursor has been used as Pr^{3+} ion source in all three pictures shown in figure 1. The OH group and Pr^{3+} concentrations are as follows:

a) 10^{-5} mol.%, 0.1 wt.%; b) 10^{-5} mol.%, 0.3 wt.%; c) 10^{-4} mol.%, 0.3 wt.%. When Pr^{3+} concentration reached 0.3 wt.% (case b), small clusters start to be formed. In the glass with higher OH group concentrations, case (c), the size and the amount of clusters increase.

Optical absorption spectrum has been recorded. OH concentration was estimated from the intensity of the 2.9 μm peak. Hydroxyle concentration ranges from 10^{-3} to 10^{-5} mol.%. Praseodymium chloride, which is

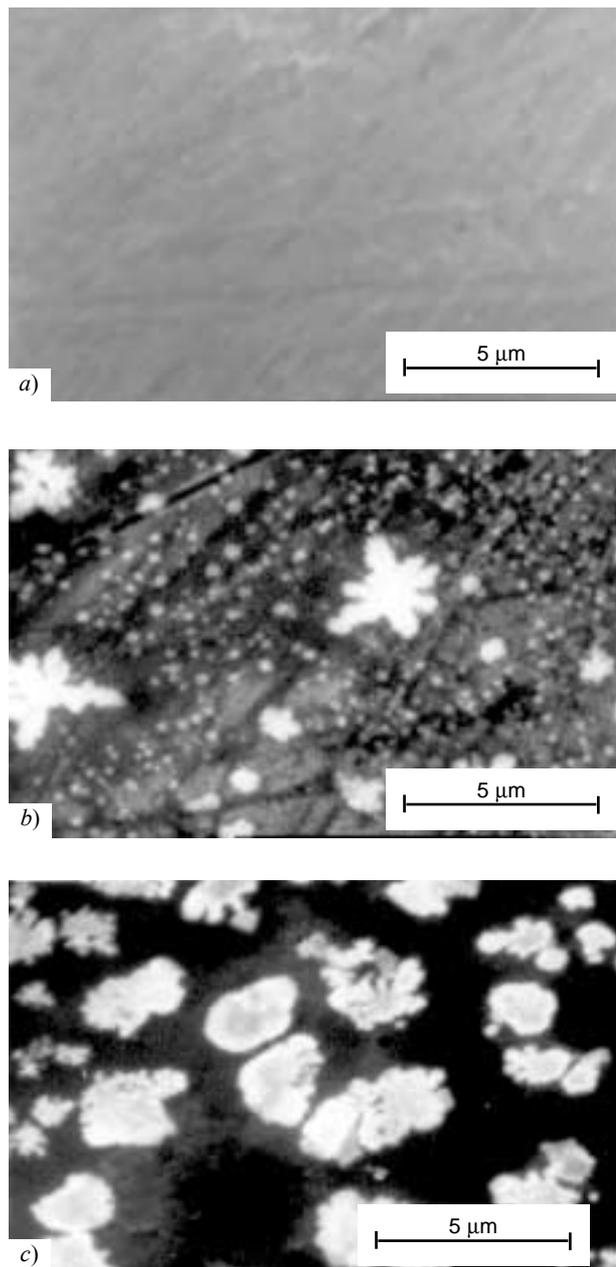


Figure 1. The SEM micrographs of $\text{Ge}_{0.25}\text{Ga}_{0.1-x}\text{S}_{0.65}\text{Pr}_x$ samples for the following OH group and Pr^{3+} concentrations.

a) 10^{-5} mol.%, 0.1 wt.%; b) 10^{-5} mol.%, 0.3 wt.%; c) 10^{-4} mol.%, 0.3 wt.%, respectively.

rather hygroscopic raises OH concentration, while it is generally low when Pr metal is used.

Raman and PL spectrometers have been used to obtain additional information on the optimal RE concentration at which the RE doped glasses are homogeneous and free of physical defects.

When the RE concentration is increased and exceeds certain limit, the mutual interaction among RE³⁺ ions starts to be significant and influences the carrier lifetime assigned to 4f inner shell electronic levels that characterise RE³⁺ ions. Thus the changes in the transition rates of intracenter electronic transitions induced by increasing RE concentration will be manifested in the intensities of both Raman and PL spectra. This concentration quenching mechanism will compete with the simple proportion - the higher the concentration of RE dopants, the higher the peak intensities originating from RE³⁺ ions and measured by Raman and PL spectrometers. The wavelengths of emission peaks measured by Raman spectrometer and corresponding peak intensities are given in tables 1 - 4, together with relevant intracenter electronic transitions for various RE elements: Pr³⁺(¹D₂→¹G₄), Nd³⁺(⁴F_{3/2}→⁴F_{13/2}), Ho³⁺(⁵I₆→⁵I₈), Dy³⁺(⁴F_{9/2}→⁶F_{3/2}), Er³⁺(⁴I_{13/2}→⁴I_{15/2}) and Sm³⁺(⁴G_{5/2}→⁶F_{11/2}).

The most detailed study has been done on samples doped with Pr and corresponding data are given for systems Ge_{0.25}Ga_{0.1-x}S_{0.65}Pr_x and Ge_{0.25}Ga_{0.05-x}As_{0.05}S_{0.65}Pr_x in tables 1 and 2, respectively. The wavelengths of the emission peaks deduced from experiments on Raman spectrometer and corresponding peak intensities are listed for various dopant concentrations and used precursor compounds. Raman intensity appears larger for samples based on the Ge-Ga-As-S glass. There is also a correlation between intensity obtained by Raman spectrometer and OH concentration. Finally, the intensity is sensitive to the rare earth precursor used - it is smaller when oxides are used as dopant sources. We can see that optimal RE concentration is around 1000 wt.ppm for Pr.

Similar conclusions could be drawn from low-temperature PL spectra of Pr doped samples shown in figure 2 for three dopant concentrations. The luminescence bands in the wavelength range 700 - 1100 nm are shown. The luminescence has been excited by the Ar ion laser (496.5 nm line). The relevant intracenter 4f transitions are indicated in the figure. We can clearly see the buildup of the crystalline phase when Pr concentration is increased above 0.1 wt.%. The crystalline phase is manifested by sharp peaks, superimposed on broad luminescence curve, characteristic of the luminescence from RE³⁺ ions embedded in the glass host. This observation correlates well with the SEM scans in figure 1 and data presented in tables 1 and 2. Concentration quenching could also be seen in figure 2.

The luminescence band around 1.33 μm, revealed by experiments on Raman spectrometer, was rather weak and noisy in our PL experiments. This was partially caused by relatively poor detection above 1.1 μm in

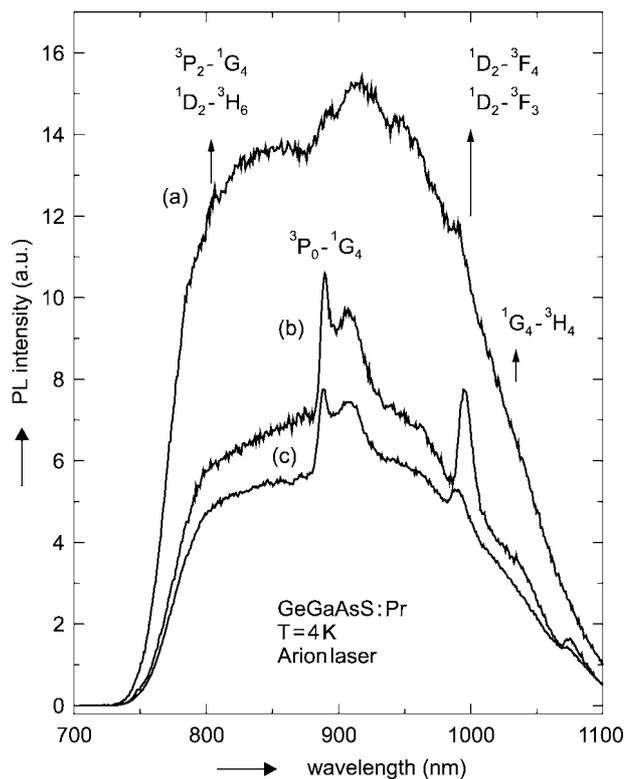


Figure 2. Low-temperature PL spectra of Ge_{0.25}Ga_{0.05-x}As_{0.05}S_{0.65}Pr_x are shown. The curves (a), (b) and (c) correspond to 0.1, 0.3 and 0.6 wt.% of Pr³⁺, respectively.

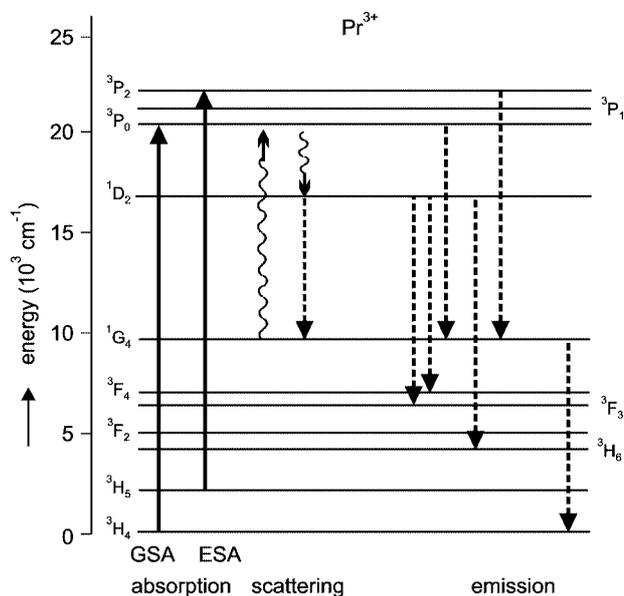


Figure 3. Schematic representation of the electronic energy levels and transitions of Pr³⁺ ion. Full lines represent the ground state (GSA) and excited state (ESA) absorption of 496.5 nm Ar ion laser. Dashed lines represent spontaneous emission processes and wavy lines represent inelastic Raman scattering of Nd:YAG laser.

Table 1. Peak intensities deduced by means of Raman spectrometer and the wavelengths of corresponding intracenter 4f transition ($^1D_2 \rightarrow ^1G_4$) are listed for various concentrations of Pr doped $Ge_{0.25}Ga_{0.1-x}S_{0.65}Pr_x$ glass samples. The content of OH group and precursor compounds used for doping are also given.

x (wt.%)	OH content (mol.%)	precursor compounds	wavelength (μm) deduced from Raman spectra $^1D_2 \rightarrow ^1G_4$	Raman peak intensity (a.u)
0.05	2×10^{-5}	Pr_2S_3	1.339	1.32
	2×10^{-5}	Pr_2O_3	1.340	0.90
	5×10^{-4}	$PrCl_3$	1.340	1.10
	8×10^{-5}	metal	1.338	2.00
	5×10^{-5}	metal	1.340	2.20
0.075	2×10^{-4}	metal	1.338	5.50
0.1	4×10^{-4}	Pr_2S_3	1.334	7.50
	4×10^{-4}	Pr_2O_3	1.338	6.90
	4×10^{-4}	$PrCl_3$	1.331	5.10
	4×10^{-4}	metal	1.342	8.10
	4×10^{-5}	metal	1.339	10.00
0.15	4×10^{-4}	metal	1.342	4.80
0.3	5×10^{-5}	Pr_2S_3	1.339	4.65
	5×10^{-4}	$PrCl_3$	1.340	3.10
	5×10^{-4}	Pr_2O_3	1.339	2.70
	8×10^{-5}	metal	1.339	5.10
0.6	8×10^{-5}	Pr_2S_3	1.341	3.80
	5×10^{-4}	$PrCl_3$	1.339	3.40
	8×10^{-5}	Pr_2O_3	1.340	2.40

Table 2. Peak intensities deduced by means of Raman spectrometer and wavelengths of corresponding intracenter 4f transition ($^1D_2 \rightarrow ^1G_4$) are listed for various concentrations of Pr doped $Ge_{0.25}Ga_{0.05-x}As_{0.05}S_{0.65}Pr_x$ glass samples. The content of OH group and precursor compounds used for doping are also given.

x (wt.%)	OH content (mol.%)	precursor compounds	wavelength (μm) deduced by Raman spectrometer $^1D_2 \rightarrow ^1G_4$	corresponding peak (a.u) intensity
0.05	2×10^{-5}	metal	1.339	6.50
	7×10^{-5}	metal	1.339	6.20
	8×10^{-5}	Pr_2S_3	1.340	5.70
	5×10^{-4}	$PrCl_3$	1.338	5.50
0.075	4×10^{-4}	metal	1.340	4.80
0.1	4×10^{-3}	Pr_2O_3	1.339	1.98
	4×10^{-4}	Pr_2S_3	1.341	6.80
	8×10^{-4}	$PrCl_3$	1.338	4.15
	8×10^{-4}	metal	1.341	10.20
	5×10^{-5}	metal	1.339	12.10
0.3	5×10^{-4}	Pr_2S_3	1.340	7.20
	5×10^{-4}	$PrCl_3$	1.336	6.90
	5×10^{-5}	metal	1.339	8.90
0.6	5×10^{-5}	Pr_2S_3	1.338	4.50

our set-up. We believe that conclusions drawn from 900 nm PL band shown in figure 2 are sufficiently general. Complementary evidence concerning the 1330 nm (1.33 μm) band is given by Raman spectroscopy.

The excitation and scattering processes in Pr^{3+} ion, that are behind the results presented in tables 1, 2 and figure 2 are schematically shown in figure 3. In the figure are shown the excitation transitions, emission bands and also the Raman scattering mediated by

Table 3. Peak intensities deduced by means of Raman spectrometer and the wavelengths of corresponding intracenter 4f transitions deduced from Raman spectra are listed for various concentrations of RE³⁺ doped Ge_{0.25}Ga_{0.1-x}S_{0.65}RE_x glass samples. Also is given the content of OH group and precursor compounds used for doping

RE ³⁺	x (wt.%)	OH content (mol.%)	precursor compounds	wavelength (μm) deduced by Raman spectrometer	corresponding peak intensity (a.u)
Pr ³⁺	0.05	5 × 10 ⁻⁵	Pr ₂ S ₃	1.339	1.32
		5 × 10 ⁻⁵	metal	1.340	2.20
	0.1	4 × 10 ⁻⁵	Pr ₂ S ₃	1.339	7.50
		4 × 10 ⁻⁵	metal	1.339	10.00
Dy ³⁺	0.05	5 × 10 ⁻⁴	Dy ₂ O ₃	1.672	0.75
	0.1	2 × 10 ⁻⁴	Dy ₂ O ₃	1.642	1.75
Ho ³⁺	0.05	1 × 10 ⁻³	HoCl ₃	1.187	0.21
	0.1	8 × 10 ⁻⁴	HoCl ₃	1.188	0.15
Nd ³⁺	0.1	8 × 10 ⁻⁴	NdCl ₃	1.363	0.038
Er ³⁺	0.05	4 × 10 ⁻⁴	ErCl ₃	1.563	0.020
	0.1	9 × 10 ⁻⁵	ErCl ₃	1.537	0.035
Sm ³⁺	0.1	5 × 10 ⁻⁴	SmCl ₃	1.476	0.030

Table 4. Peak intensities deduced by means of Raman spectrometer and the wavelengths of corresponding intracenter 4f transitions deduced from Raman spectra are listed for various concentrations of RE³⁺ doped Ge_{0.25}Ga_{0.05-x}As_{0.05}S_{0.65}RE_x glass samples. Also is given the content of OH group and precursor compounds used for doping.

RE ³⁺	x (wt.%)	OH content (mol.%)	precursor compounds	wavelength (μm) deduced by Raman spectrometer	corresponding peak intensity (a.u)
Pr ³⁺	0.05	2 × 10 ⁻⁵	Pr ₂ S ₃	1.340	5.70
		2 × 10 ⁻⁵	metal	1.339	6.50
	0.1	5 × 10 ⁻⁵	Pr ₂ S ₃	1.341	6.80
		4 × 10 ⁻⁵	metal	1.339	12.10
Dy ³⁺	0.05	4 × 10 ⁻⁴	Dy ₂ O ₃	1.672	1.00
	0.1	2 × 10 ⁻³	Dy ₂ O ₃	1.673	2.25
Ho ³⁺	0.05	1 × 10 ⁻³	HoCl ₃	1.187	0.30
	0.1	8 × 10 ⁻⁴	HoCl ₃	1.187	0.48
Nd ³⁺	0.1	9 × 10 ⁻⁴	NdCl ₃	1.360	0.06
Er ³⁺	0.05	4 × 10 ⁻⁴	ErCl ₃	1.537	0.02
	0.1	4 × 10 ⁻⁴	ErCl ₃	1.537	0.04
Sm ³⁺	0.1	5 × 10 ⁻⁵	SmCl ₃	1.476	0.03

energy levels responsible for emission band 1.33 μm indicated in tables 1 and 2.

A second group of samples has been prepared using other RE as doping elements: Dy, Ho, Er, Nd and Sm. Corresponding data are gathered in tables 3 and 4. Lanthanide concentration was 0.05 or 0.1 wt.%.

DISCUSSION

Results presented above show that RE cations may be incorporated without change in optical quality when doping concentration does not exceed 0.15 wt.%. This level is sufficient for most fibre applications.

In Pr-doped glasses, Raman intensity varies significantly from sample to sample and also as Pr concentration increases. For a given Pr content, e.g. 0.05 wt.%, it depends on OH concentration. The quenching effect of hydroxyles on the ¹D₂ → ¹G₄ transition has already been outlined and has a drastic influence on the fluorescence life time. In this set of experiments, lifetimes were not measured.

Fluorescence and Raman intensity depends both on the number of active ions, that is their concentration, and also on radiative lifetime. As far as concentration quenching is negligible, i.e. at low rare earth content, intensity increases with Pr concentration. Thus it is

lower at 0.05 wt.% than at 0.1 wt.%. At higher Pr concentration, quenching becomes too large, which leads to the decrease of the fluorescence intensity, despite the large number of Pr³⁺ ions.

Certain trend in the influence of the doping precursor anion may also be seen. Fluorescence intensity is smaller at 0.05, 0.1 and 0.3 wt.% when Pr₂O₃ is used instead of Pr₂S₃, although OH concentration is similar. This suggests that anionic oxygen, which is introduced together with Pr is not diluted in the vitreous matrix, but in some way remains near the rare earth, raising the local phonon energy. A similar, but reverse, effect was observed when heavier halides are used as dopants in fluoride glasses. It is more difficult to assess precisely the influence of chlorine anions in sulphide glasses. Fluorescence intensity is generally lower when PrCl₃ is used in place of Pr₂S₃ or Pr metal. But OH concentration is also higher in most cases. In addition, one may expect that water contamination arising from PrCl₃ itself will result in the formation of OH groups in the vicinity of the rare earth. This implies that glass is not the homogenous material one would expect ideally, but this is still a matter of discussion.

The practical interest of rare earth doped sulphide glasses lies in the development of fibre devices. Fibre drawing ability in these systems has been demonstrated a long time ago. Further problems arise from the need of using single mode fibres, for optical amplification and for fibre lasers. It is often assumed that high fibre losses may be tolerated if gain is large. However, it is clear that impurity content should be very small. Also scattering makes serious problems both in amplifiers and lasers. As a consequence, the specifications for active and passive fibres become closer. Sulphide fibres should be developed for diode pumped solid state lasers operating at wavelengths larger than 3 μm. In the mean time, optimised sulphide fibres could be used in sensing and remote spectroscopy beyond 4 μm.

CONCLUSIONS

Rare earth cations have been incorporated in germanium sulphide glasses. Lanthanide precursors were oxides, sulphides, chlorides or metal. More systematic synthesis were carried out with praseodymium. Glass samples are homogeneous and free of crystals when rare earth concentration is lower than 0.15 wt.%. Hydroxyl concentration could be lowered in the 10⁻³ to 10⁻⁵ range. Both OH content and doping precursors have a significant influence on emission intensity as estimated from measurements on Raman spectrometer. These glasses may be drawn into fibers, leading to potential applications as passive or active fibers. PL spectroscopy proved to be a very precise technique to reveal the RE concentration beyond which the crystalline phase starts to build up. Investigation of RE³⁺ electron energy levels by means of Raman spectrometer yields complementary information about radiative transitions beyond 1 μm.

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SULFIDOVÁ SKLA DOTOVANÁ PRVKY VZÁCNÝCH ZEMIN

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Některá sulfidová skla především Ge-Ga-S a Ge-Ga-As-S systémů dopovaná ionty vzácných zemin RE jako Pr, Er, Nd, Ho, Dy apod. jsou materiály potřebné pro různé fotonické aplikace zejména jako laserová aktivní optická vlákna. Jejich výhodou oproti křemičitým sklům je jejich nižší hodnota fononové energie, vyšší hodnota indexu lomu (nad 2) a propustnost záření ve střední infračervené oblasti spektra. Protože rozpustnost iontů vzácných prvků je do značné míry ovlivněna čistotou základního skla, zejména koncentrací OH skupin, pozornost byla nejprve věnována přípravě vysoce čistých a homogenních nedotovaných a dotovaných skel o složení Ge_{0,25}Ga_{0,05-x}As_{0,05}S_{0,65}RE_x a Ge_{0,25}Ga_{0,1}S_{0,65}RE_x pro x = 0,05; 0,1; 0,3; 0,6 hmotn.%. Připravená skla byla studována infračervenou absorpční spektrometrií, chemickou a RTG strukturální analýzou, elektronovým skanovacím mikroskopem, fotoluminiscenční spektroskopii při nízkých teplotách. Na základě uvedených měření byla nalezena závislost mezi hodnotami koncentrací OH skupin, iontů vzácných zemin a vznik klastřů v základním skle. Ukázalo se, že zatím nejvhodnějším dopantem jsou Pr ionty o koncentraci 0,1 hmotn.% při koncentraci OH iontů pod 10⁻⁴ mol.%.