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# Special glasses for infrared applications

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Selected sulphide, selenide and telluride glass systems together with $TeO_2$ based heavy metal oxide ones have been prepared and investigated by SEM and low-temperature photoluminescence spectroscopy. Glasses without crystalline particles, clusters and chemical inhomogeneities have been prepared by direct synthesis from pure starting elements and compounds. Homogeneity of rare earth (Pr, Er) doped glasses depends on the kind of $RE^{3+}$ ions, their concentration and chemical forms in which they were added. We have investigated the 4f-4f inner shell radiative transitions of $Er^{3+}$ and $Pr^{3+}$ ions incorporated into various glass hosts. All relevant radiative transitions of $Er^{3+}$ and $Pr^{3+}$ have been observed in GeGaS and GeGaAsS systems. As far as Er is concerned the same applies to $As_2S_2Se$ and $As_2Se_3$ glass systems, while only a peculiar $Pr^{3+}$ transition at 1590 nm is seen in these selenide systems. Er doped tellurides exhibit strong luminescence of $Er^{3+}$ at 1539 nm while only a weak peak at 1590 nm has been found for Pr doped ones. No restriction of $Pr^{3+}$ radiative transitions is observed in $TeO_2$ related heavy metal oxide glass systems.

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## 1. Introduction

There is a growing interest in the family of special glasses, particularly chalcogenide and heavy metal oxide (HMO) ones, due to there promising properties such as transmission in middle and far infrared (IR) region of spectra, lower values of phonon energies and higher values of refraction index as compared to $SiO_2$ [1, 2]. These glasses and corresponding optical fibres can be used as passive elements in power delivery or imaging systems.

Active devices based on the spectroscopic properties of rare earth (RE) cations (the screened 4f shell) are the subject of numerous studies [2] for potential applications in the field of optoelectronics. Of particular interest are optical amplifiers for telecommunications and fibre lasers. Also active planar waveguides make an attractive option for integrated optics.

First developments related to RE addition have been tested on classical materials such as silica fibres [3]. 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 to accommodate RE ions 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 excited RE energy 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 predomimant.

Thus, since silica phonon energy is too large for 4f-4f inner shell 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 [4, 5]. 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 RE cations are difficult to incorporate into these glasses, probably for structural reasons. We have observed that lanthanide solubility is enhanced when gallium is included in the base glass composition. In this contribution we report the preparation of selected sulphide, selenide and telluride glass systems together with $TeO_2$ based HMO ones, and their characterisation by low-temperature photoluminescence (PL) spectroscopy. In particular we concentrate on the radiation efficiency of erbium (Er) and praseodymium (Pr) ions in various glass hosts.

## 2. Experimental

Sulphide (GeGaS, GeGaAsS), selenide ($As_2Se_3$, $As_2S_2Se$) and selenide–telluride (GeSeTe) glasses were prepared by direct synthesis from pure starting elements and compounds. The required chemical and physical purity of prepared glasses is about $10^{-5}$ mol % for the presence of OH, SH, SeH groups and the concentration of physical defects in the range $10^2$ - $10^3$ per cm$^3$. The major sources of hydride and carbon impurities seem to be starting elements (As, Ge, S, Se, Te) and therefore re-purification of these elements must be carried out. The sublimation under vacuum and the reactive atmosphere proved to be very effective for S, Se, Te, As and melting under vacuum showed similar effects for Ge and Ga. 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 [6]. 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 and Ga about 850 - 950 °C. The melting time was 15 - 20 hours and then the ampoule with glass melt was cooled to room temperature. Preforms of 10 mm in a diameter and 50 – 80 mm in length were obtained. The concentration of Pr and/or, Er ranges from 500 to 3000 wt.ppm, and sulphide, oxide, chloride or elemental form were used for the dotation

Samples on the base of $TeO_2$ related glass systems have been treated at 230°C in a flow of oxygen and reactive atomic chlorine atmosphere (obtained by decomposition of $CCl_4$ at 800°C) in order to remove the moisture from their surface. Melting of the mixtures in Pt crucibles was carried out for 20 minutes at the temperatures in the range 750-820°C. Subsequently the glass melt was poured into forms having 8 mm in diameter and 35 - 50 mm in length. Prepared glasses were annealed at 200°C for 1 hour and then slowly cooled to room temperature. After annealing samples were cut and polished to optical quality. Glasses whose composition was stable against devitrification were doped with Pr and Er by using various precursors.

Prepared glasses have been examined by SEM equipped with EDX system, absorption spectroscopy, and low-temperature photo-luminescence (PL) spectroscopy. Transmission spectra in the visible range have been measured by Specord M400 and in NIR by Matson Galaxy 3000. Photoluminescence spectra were taken at various temperatures and various levels of excitation by He-Ne, Ar-ion and 830 nm LD lasers in the optical closed-cycle He cryostat enabling measurements in the temperature range 3.5-300 K. The 1 m focal length monochromator coupled with thermoelectrically cooled GaAs photomultiplier and liquid nitrogen cooled high-purity Ge detection system enables sensitive and high resolution measurements in the spectral range 400 – 1700 nm by using lock-in technique.

## 3. Results and discussion

Prepared sulphide glasses are yellow-orange or red (with arsenic) coloured, and they also exhibit the characteristic absorption bands of RE cations. No visible defects or crystalline phase are seen under microscope. Results obtained by SEM could be summarised as follows:

- Base glasses $Ge_{0.25}Ga_{0.1}S_{0.65}$ and $Ge_{0.25}Ga_{0.05}As_{0.05}S_{0.65}$ appear homogeneous and free of crystalline inclusions
- The homogeneity of the samples containing RE ions (Pr, Er,) 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 $Ge_{0.25}Ga_{0.1-x}S_{0.65}Pr_x$ samples are shown in Fig. 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 Fig. 1. The OH group and $Pr^{3+}$ concentrations are as follows: (a) $10^{-5}$ mol%, 1000 wt.ppm; (b) $10^{-5}$ mol%, 3000 wt.ppm; (c) $10^{-4}$ mol%, 3000 wt.ppm. When $Pr^{3+}$ concentration reached 3000 wt.ppm, 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.

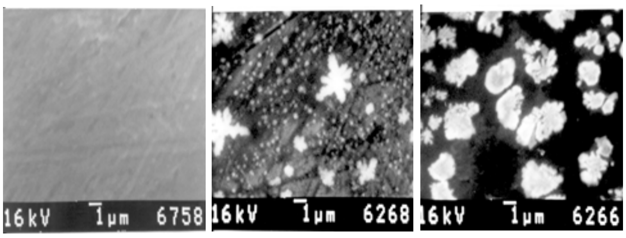

*Fig. 1. The SEM micrographs of $Ge_{0.25}Ga_{0.1-x}S_{0.65}Pr_x$ samples for the following OH group and $Pr^{3+}$ concentrations, (a) $10^{-5}$ mol%, 1000 wt.ppm; (b) $10^{-5}$ mol%, 3000 wt.ppm; (c) $10^{-4}$ mol%, 3000 wt.ppm are shown, respectively.*

The 4f-4f inner shell radiative transitions of $Er^{3+}$ and $Pr^{3+}$ ions incorporated into various glass hosts have been investigated by low-temperature PL spectroscopy. PL spectra have been measured in wide temperature range by using He-Ne (632.8 nm), Ar ion (514.5 nm) and semiconductor diode (830 nm) for excitation. In the case of GeGaS and GeGaAsS systems all relevant (in the measured range 800 to 1700 nm) radiative transitions of both $Er^{3+}$ and $Pr^{3+}$ ions have been observed. In the case of Er doping the same applies to $As_2S_2Se$ and $As_2Se_3$ glass systems, while only a peculiar $Pr^{3+}$ transition at 1590 nm is seen in these systems. Typical PL spectra of $Ge_{0.25}Ga_{0.05}As_{0.05}S_{0.65}$ system doped with Er and Pr are shown for three temperatures in Fig. 2 and 3, respectively.

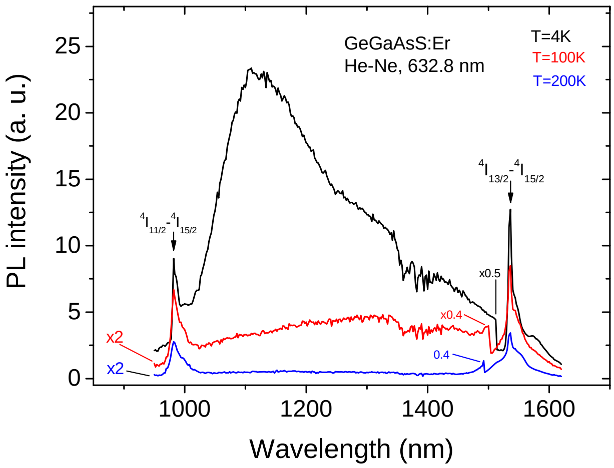

*Fig. 2. PL spectra of GeGaAsS:Er (1000 wt.ppm) are shown for three temperatures. Both relevant $Er^{3+}$ transitions, superimposed are clearly seen.*

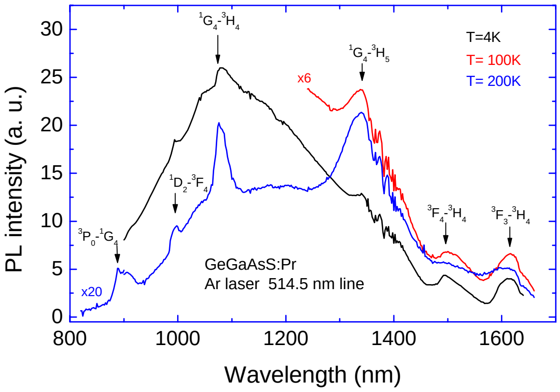

*Fig. 3. PL spectra og GeGaAsS:Pr (750 wt.ppm) are shown for three temperatures. All relevant $Pr^{3+}$ transitions, superimposed on the base glass luminescence are seen together with a distorted transition at 1600 nm.*

The observed sharp inner shell transitions of RE ions are superimposed on the broad luminescence curve due to radiative transitions in the base glass .The base glass luminescence is considerably increased with decreasing temperature and shifts towards lower energies. The large difference between the PL peak and the band gap ($E_g$) is the indication that deep states are involved in the recombination. Kolomiets suggested [7] that observed transitions are from band tails to states near the middle of the forbidden gap. The broadening of the luminescence band can be explained as due to electron–phonon interaction. The model of strong electron-phonon coupling as introduced by Street [8] well describes PL spectra observed in chalcogenide semiconductors and enables to estimate the corresponding Stokes shift by simultaneous measurements of PL and absorption spectra.

RE related transitions are more pronounced at elevated temperatures since the base glass luminescence decays rapidly near the room temperature while 4f–4f transitions depend little on temperature.

PL spectra of selenide–telluride multi–component alloys doped with Er and Pr have been measured at various temperatures. Er doped tellurides exhibit only luminescence at 1539 nm and just a weak peak at 1590 nm has been found for Pr doped ones. Low temperature PL spectra of $Ge_{20}Se_{80-x}Te_x$:Er system are shown in Fig. 4. It turns out that only the ${}^4I_{13/2}\rightarrow{}^4I_{15/2}$ radiative transition is efficient in this system. Besides, the shift of the dominant base glass luminescence band from 1200 nm ($Ge_{20}Se_{80}$), to 1550 nm ($Ge_{20}Se_{70}Te_{10}$) could be seen. The structure at about 1350 nm is due to the absorption of emitted luminescence by water vapour in the air. It is seen because there is a strong signal within the water vapour absorption edge. The asymmetry of the spectral shape for higher Te content is caused by the cut off of the Ge detection system beyond 1700 nm.

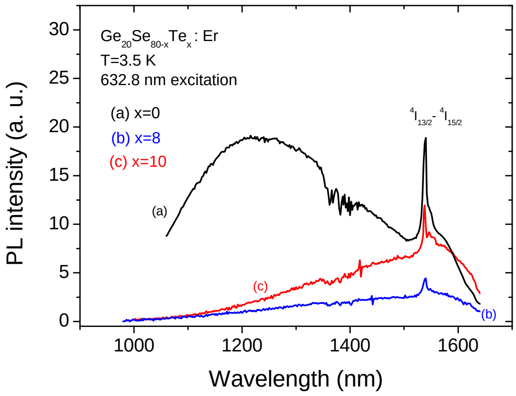

*Fig. 4. Low temperature PL spectra of $Ge_xSe_{80\text{-}x}Te_x$ doped with Er (1000 wt.ppm) are shown for x=0, 8 and 10. Only the dominant 4f-4f transition of $Er^{3+}$ at 1539 nm is clearly seen.*

The efficiency of $Pr^{3+}$ radiative transitions in glasses prepared from GeSe by As or Te substitution is demonstrated in Fig. 5, where GeAsSe and GeSeTe with and without Pr doping are compared. The observed peak at 1590 nm could be assigned to the peculiar ${}^3F_3\rightarrow{}^3H_4$ transition of $Pr^{3+}$ ion.

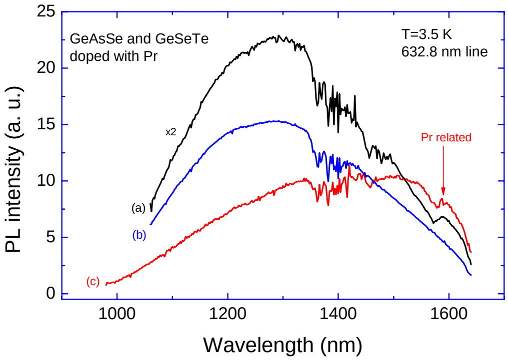

*Fig. 5. Low temperature base glass luminescence is shown together with the peculiar ${}^3F_3\rightarrow{}^3H_4$ transition of $Pr^{3+}$ ion at 1590 nm. The curves (a), (b) and (c) correspond to $Ge_{20}As_{15}Se_{65}$:Pr, $Ge_{20}As_{15}Se_{65}$ and $Ge_{20}Se_{73}Te_7$:Pr glass systems, respectively.*

In view of the higher phonon energies in HMO glasses as compared to chalcogenide ones it is surprising that in $TeO_2$ based systems all 4f–4f transition of Er and Pr ions have been observed. Temperature dependence of PL spectra for $(TeO_2)_{70}(ZnO)_{30}$:$Pr_2O_3$ is shown in Fig. 6 for the temperature range 100-300 K. Since the RE related luminescence transitions exhibit considerably smaller dependence on temperature in comparison with the base glass luminescence, only the strongest $Pr^{3+}$ transition is properly seen at liquid He temperature.

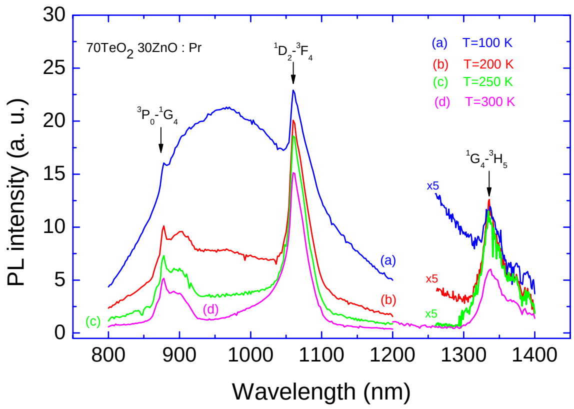

*Fig. 6. Temperature dependence of PL spectra for* $(TeO_2)_{70}(ZnO)_{30}$:$Pr_2O_3$ *is shown. 4f→4f inner shell transitions from* $Pr^{3+}$ *ions, i.e.* $^3P_0 \rightarrow {}^1G_4$ *at 880 nm,* $^1D_2 \rightarrow {}^3F_4$ *at 1060 nm and* $^1G_4 \rightarrow {}^3H_5$ *at 1330 nm, are indicated by arrows.*

## 4. Conclusions

Pure undoped and homogeneous sulphide, selenide and selenide–telluride glasses without crystalline particles, clusters and chemical inhomogeneities have been prepared. Homogeneity of RE (Pr, Er) doped systems depends on the kind of $RE^{3+}$ ions, their concentration and chemical forms in which they were added (sulphides, oxides, chlorides and metal).

All allowed radiative transitions of $Er^{3+}$ and $Pr^{3+}$ ions have been observed in GeGaS and GeGaAsSe systems. Relevant $Er^{3+}$ transitions are also observed in $As_2S_2Se$ and $As_2Se_3$ glasses, while only a peculiar $Pr^{3+}$ transition at 1590 nm is seen in these systems. Er doped tellurides exhibit strong luminescence of $Er^{3+}$ ion at 1539 nm and only a weak peak at 1590 nm is found in Pr doped ones. No restriction of $Pr^{3+}$ radiative transitions is observed in $TeO_2$ related HMO glass systems–$(TeO_2)_{70}(ZnO)_{30}$, $(TeO_2)_{60}(PbCl_2)_{40-x}(PbF_2)_x$. Thus we conclude that GeSeTe systems together with studied selenide ones do not support radiative transition $^1G_4 \rightarrow {}^3H_5$ of $Pr^{3+}$ at 1340 nm but a relatively weak luminescence peak at 1590 nm is observed in all investigated selenide and telluride systems. We tentatively assign the band at 1590 nm to $^3F_3 \rightarrow {}^3H_4$ transition of $Pr^{3+}$ ion. A distinct shift of the dominant base glass luminescence band towards longer wavelength has been observed in $Ge_{20}Se_{80-x}Te_x$ glasses with increasing Te content.

### Acknowledgement

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