



Low-temperature photoluminescence in chalcogenide glasses doped with rare-earth ions



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ABSTRACT

Sulfide and oxysulfide bulk glasses Ga-La-S-O, Ge-Ga-S and Ge-Ga-As-S doped, or co-doped, with various rare-earth (RE^{3+}) ions are investigated for their room temperature transmission and low-temperature photoluminescence. Photoluminescence spectra are collected by using external excitation into the Urbach tail of the fundamental absorption edge of the host-glass. The low-temperature photoluminescence spectra are dominated by the broad-band luminescence of the host glass, with superimposed relatively sharp emission bands due to radiative transitions within $4f$ shells of RE^{3+} ions. In addition, the dips in the host-glass luminescence due to $4f$ - $4f$ up-transitions of RE^{3+} ions are observed in the Ge-Ga-S and Ge-Ga-As-S systems. These superimposed narrow effects provide a direct experimental evidence of energy transfer between the host glass and respective RE^{3+} dopants.

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1. Introduction

Some unique optical properties of chalcogenide glasses make them interesting for optoelectronic devices in the visible (VIS) and, especially, in the near- and mid-infrared (NIR and MIR) spectral regions. Sulfide glasses are promising hosts for rare-earth (RE^{3+}) ions for photonic applications such as fibre lasers, optical amplifiers and up-convertors, in which radiative electronic transitions between discrete energy levels of RE^{3+} ions can be exploited. This is due to the low phonon energy, extended MIR transparency and high refractive index of the host-glass, resulting in high spontaneous emission probabilities, large emission cross-sections and low non-radiative decay rates between energy levels of the doped-in RE^{3+} ions. The host-glass low phonon energy is of particular importance for obtaining a high quantum efficiency of the radiative transitions of the dopant RE^{3+} ions, by reducing the probability of non-radiative energy transfer from the excited RE^{3+} ions into the surrounding host-glass matrix. This results in the observation of many MIR transitions of the RE^{3+} ions doped into chalcogenide

glasses that are normally not present in host materials of higher phonon energy. In addition, the long-wavelength vibrational absorption edge of sulfide glasses is shifted towards longer wavelengths in comparison with oxide and halide glasses. Sulfide glasses have, in the past, been proposed as a potential host material for λ (wavelength) = 1.3 and 1.5 μm optical fibre amplifiers and, more recently, as fibre lasers in the NIR and MIR spectral regions and for planar waveguides and ultrafast optical nonlinear devices [1–5].

Generally, the solubility of RE^{3+} ions in chalcogenide glasses is quite low. But it has been shown that the addition of gallium (Ga^{III}) [6–9] into chalcogenide glasses can significantly increase the solubility of RE^{3+} ions. A high solubility of RE ions is important not only for fundamental spectroscopic studies but also for the preparation of active photonic devices, exploiting RE ion doped glasses. It has been found that Ge–Ga–S glasses are especially characterized by a high Er^{3+} solubility, in comparison with other chalcogenide glass systems; on addition of Ga into the Ge–S glass [10] a local structural modification occurs, allowing better incorporation of the RE^{3+} ions in the glass matrix. The Ga–La–S system also exhibits a high solubility of active RE ions, because of the easy substitution of La by other RE ions in the glass structure.

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The sulfide glasses Ge-Ga-S, Ge-Ga-As-S and Ga-La-S are all good host materials for active RE ions. They have large glass forming regions, are highly transmissive in the visible, NIR and MIR regions of the spectrum, exhibit a wide range of the forbidden band-gap, $E_g \approx 2.0\text{--}2.6$ eV, a high refractive index ($n = 2.4\text{--}2.5$ at $\lambda = 0.63$ μm), sufficiently good mechanical and chemical durability and high values of the glass transition temperature: $T_g\text{--}400\text{--}550$ °C. It has been demonstrated that the introduction of oxide into Ga-La-S glasses [2,11] and As into Ge-Ga-S [12,13] plays an important role in preventing devitrification during processing of these glasses (by the so-called: “confusion principle”). However, the addition of oxide significantly raises the average phonon energy of the Ga-La-S-O glasses relative to the Ga-La-S glasses.

We have previously reported on absorption and photoluminescence (PL) spectra in the VIS region obtained for Ga-La-S-O and Ge-Ga-As-S glasses doped with RE^{3+} ions [2,11–14]. In the present paper, we report the optical transmission spectra in the VIS and NIR regions, at room temperature, and low-temperature PL spectra measured in the NIR range for Ga-La-S-O, Ge-Ga-S, and Ge-Ga-As-S glasses doped with various RE^{3+} ions. Data obtained using room temperature transmission spectroscopy in the range of 400–1100 nm are reported in order to monitor the position of the fundamental electronic absorption edge of these different glasses. We focus on the low-temperature PL spectra in the NIR range to complement our previous investigation of these systems at room temperature in the wavelength range mostly not exceeding 900 nm [2,11,13,14]. Another reason to focus on the low-temperature PL in the NIR range is our previous experience with low-temperature PL spectra collected from various glass systems doped with RE^{3+} ions [15–17].

The NIR range is of interest since it enables simultaneous observation of the host-glass luminescence with superimposed effects due to $4f\text{--}4f$ transitions within RE^{3+} ions doped into the host glass. The broad-band host-glass PL, mediated by the presence of deep energy states in the band-gap, centred at about the mid-band-gap energy, is strongly dependent on temperature, and it is usually observed only at low-temperature [18–21]. On the other hand, the $4f\text{--}4f$ inner shell transitions exhibit little temperature dependence and are readily observed at room temperature. The wavelength range where the host-glass broad-band PL overlaps some of the $4f\text{--}4f$ transitions of the doped-in RE^{3+} ions is of particular interest. In this range it is possible to observe simultaneously the broad-band PL with the superimposed, relatively narrow effects due to the RE^{3+} ions $4f\text{--}4f$ transitions.

Here, we have used excitation wavelengths that were not resonant with $4f\text{--}4f$ transitions of the doped-in RE^{3+} ions but had reasonable overlap with the Urbach absorption tail of the host glass. In fact, a previous study of Pr^{3+} doped sulfide glasses [20] concluded that it is advantageous to use an external excitation source that assures the higher absorption coefficient for the glass matrix as compared to doped-in RE^{3+} ions, if the observation of the broad-band PL in glasses doped with RE^{3+} ions is desired.

In this contribution we would like to demonstrate on a wide range of chalcogenide glasses and RE^{3+} ions that simultaneous observation of the photoluminescence due to electronic transitions in the host glass and due to electronic transitions within $4f$ shells of doped-in RE^{3+} ions is of importance and provides a new insight into the energy transfer within the RE doped glass systems. These narrow features superimposed on the host-glass low-temperature PL spectra that are related to energy transfer have been observed in our laboratory [15–17] and also by other authors [22,23] previously in several chalcogenide and heavy metal oxide glass systems doped with RE^{3+} ions. However, these observations were so far presented in a scattered way without proper discussion. In this study, not only characteristic emissions of the RE^{3+} ions, superposed on the host-

glass broad-band PL, were observed, but we have also observed in tandem characteristic dips in the host-glass broad-band PL, that are related to electronic transitions in RE^{3+} dopants. These relatively narrow dips in the broad-band host-glass PL observed by us at low-temperature represent one possible channel for electronic interaction or exchange of energy between the host-glass and $4f$ electrons of RE^{3+} ions.

2. Experimental

One oxysulfide and two sulfide glass systems were investigated in this study viz.: Ga-La-S-O, Ge-Ga-S and Ge-Ga-As-S. The compositions of glasses are referred to initial batch mixtures. The semi-quantitative electron diffraction X-ray (EDX) analysis was used to verify the composition of prepared samples. The difference between nominal (batch mixture) and real glass composition found on series of samples prepared by the further described methods were found to be smaller than precision of EDX analysis (to $\pm 2\%$ relative to major components). Oxygen content was assumed being the same in prepared glass as in the batch [24,25].

The Ga-La-S-O glasses doped with Pr^{3+} were prepared by melting standard sulfides and oxide (Merck Ltd) at 1150 °C for 5 h in a vitreous carbon crucible inside a silica-tube. The $(\text{Ga}_2\text{S}_3)_{70}\text{--}(\text{La}_2\text{S}_3)_{30}$ glass was modified by partial substitution of La_2S_3 with La_2O_3 in the ratio of 26:4 and 13:17, leading to two concentrations of (O) roughly equal to 0.65 and 2.95 wt%, respectively. These glasses are further referred to as GLS: x (O): y [Pr], where x and y are the weight percentage (wt%) of (O) and atomic percentage (at%) of [Pr], respectively. The Pr^{3+} concentration y in starting mixture was 0.1 at% and 1.0 at%, respectively.

The RE^{3+} doped Ge-Ga-S glasses were prepared by the conventional chalcogenide glass melting technique. Respective melts were prepared using slightly different approaches – the Er^{3+} -doped glasses were prepared starting from mixtures of sulfides (GeS_2 , Ga_2S_3 and Er_2S_3), while those doped with Pr^{3+} were prepared directly from the pure elements (Ge, Ga, S, Pr). The glasses for both types were prepared in evacuated ($\sim 10^{-3}$ Pa) silica-glass ampoules which were heated up to 1000 °C at $2\text{--}4$ °C min^{-1} , employing a stepwise regime (involving a 2 h isothermal hold at each of 250, 550 and 750 °C). Then the melt was quenched, *in situ*, inside the evacuated silica-glass ampoule, in ice-water. In the case of Er-doping, the composition was $[(\text{GeS}_2)_{80}\text{--}(\text{Ga}_2\text{S}_3)_{20}]_{100\text{--}z}[\text{Er}_2\text{S}_3]_z$, where $z = 0.3$ and 2.1 mol% Er_2S_3 . This composition is based on $(\text{GeS}_2)_{80}\text{--}(\text{Ga}_2\text{S}_3)_{20}$, i.e. ratio between GeS_2 and Ga_2S_3 is 4:1, which roughly corresponds to $\text{Ge}_{235}\text{Ga}_{118}\text{S}_{647}$ composition [26]. The preparation of Pr^{3+} doped Ge-Ga-S glasses (1000 wt.ppm of Pr ~ 0.033 at% of Pr) by direct synthesis from pure elements was described previously [12]; the base glass composition corresponds to $\text{Ge}_{25}\text{Ga}_{10}\text{S}_{65}$ (at%), i.e. ratio between GeS_2 and Ga_2S_3 is 5:1. Both types of glasses within the system of Ge-Ga-S are further referred to here as GGS glasses.

RE^{3+} doped Ge-Ga-As-S glasses were prepared from high purity (6 N) elements – Ga, Ge, As, S – and the rare earth metal (viz. Pr, Dy, Nd, Sm and Ho) inside evacuated silica-glass ampoules, and heating at 927 °C for 30 h in a rocking furnace and then quenching *in situ*, in water. The base glass was $\text{Ge}_{250}\text{Ga}_{17}\text{As}_{83}\text{S}_{650}$ (at%), which will be referred to here as GGAS glass. GGAS glasses were either singly doped with 0.05 and 0.2 at% Pr^{3+} , 0.05 and 0.2 at% Dy^{3+} , 0.05 and 0.2 at% Nd^{3+} , 0.05 and 0.2 at% Sm^{3+} , or co-doped with 0.2 at% of $(\text{Ho}^{3+} + \text{Dy}^{3+})$ admixtures, with two Ho: Dy atomic ratios of 0.13: 0.07 and 0.07: 0.13, respectively. Dopants were added to the base glass keeping the base glass molar ratio constant for the different amounts of RE ions.

For all of the prepared glasses, samples of about 2 mm thickness were cut from the as-annealed ingots and polished under non-

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