



Near-IR emission of Er³⁺ ions in CsCl-Ga-Ge-S glasses excited by visible light



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ABSTRACT

Fluorescence of 65GeS₂-25Ga₂S₃-10CsCl glasses doped with Er has been investigated at room and liquid nitrogen temperatures. Strong emission lines at ~1 and ~1.5 μm are observed at room temperature in Er-doped samples when excited with ~530 nm wavelength. At cryogenic temperature, this fluorescence is observed even at lower excitation wavelengths (~400–450 nm). The other observed emission and absorption lines agree well with known energy level transitions of Er³⁺ ions incorporated in the glass matrix and temperature behavior of absorption spectra. The difference between room and liquid nitrogen temperature up-conversion emission is observed under femtosecond pulsed 800 nm laser excitation.

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1. Introduction

Chalcogenide glasses have been deemed desirable for many applications because of their wide infrared (IR) transmission windows, high refractive indexes, low multiphonon reactions, photostructural effects, favorable thermal properties and capability to operate at high power, especially at low phonon energy [1,2]. They are easier to synthesize and shape compared to crystalline materials, which makes them more efficient and inexpensive to produce. The combination of these unique properties with good rare-earth solubility also allows the application of chalcogenide glasses in optical sensing, as active media for lasers, optical amplifiers and broad band sources in the mid-IR spectral range, which rely on rare-earth dopant transitions that occur in the high transmission window of the host glass [3–10].

The CsCl-modified Ga-containing germanium sulfide glasses provide one of the best host matrixes for rare-earth elements [4,5]. Their transmission window covers the ~475 nm–12 μm spectral

range, where thermal infrared imaging becomes relevant [5,6]. When the alkaline halide CsCl is added to Ga-Ge-S glass stoichiometrically (up to 50 mol.%), the material's optical transmission can be extended further into the short-wave light region up to ~425 nm [7–9]. This drastically increases the possibility for the excitation of rare-earth ions in the glass. Among a variety of rare-earth elements, doping with Er³⁺ ions attracts attention mostly because of ⁴I_{13/2} → ⁴I_{15/2} ground state transition occurring around 1.55 μm – a standard telecommunication wavelength [9]. Typically, Ga-Ge-S glasses will dissolve up to ~1 at. % of Er³⁺ [10], which makes them supreme candidates for IR optical fibers and waveguides used in telecommunications [4,5,11].

In this paper, the room and cryogenic temperature fluorescence in CsCl modified Ga-Ge-S glasses doped with Er is studied. The effect of temperature helps to reveal peculiarities of Er³⁺ transitions in the above glass matrix, which will allow further engineering of these materials and tailoring for specific applications.

2. Experimental

The Er-doped (0.6 and 1.0 at.%) 65GeS₂-25Ga₂S₃-10CsCl glasses were prepared through a standard melt-quench method. Pure raw 5N materials (Ge, Ga, S, CsCl and Er in metallic form) were melted at

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890–930 °C in evacuated silica ampoule for 12 h before being quenched from 850 °C in a cold water. Special purification procedures were used to obtain high purity glass, as described by Masselin et al. [9]. Glasses were annealed at $T_g - 15$ °C for 5 h in order to minimize the mechanical strains produced during the quench. Then, the samples were cut into 1 mm thick disks (8 mm in diameter) and polished for optical measurements.

The fluorescence spectra were measured at room ($T_R = 298$ K) and liquid nitrogen ($T_{LN} = 77$ K) temperatures using Horiba Fluorolog-3 spectrofluorimeter equipped with xenon short arc lamp as a light source. The 300–950 nm wavelengths range was used for excitation, while the emission spectra were collected in the 970–1600 nm range using liquid nitrogen cooled Horiba Jobin Yvon InGaAs DSS-IGA020L detector. A special two-layer fused silica glass Dewar assembly (Horiba FL 1013), which is transparent in the visible and infrared regions of spectrum, was used for measurements at cryogenic temperature. The Dewar was filled with liquid nitrogen (LN) and the samples were completely submerged in LN throughout the entire measurement period.

Optical transmission in the fundamental optical absorption region was measured using Avantes AvaSpec spectrometer equipped with a halogen light source. Transmission at cryogenic temperature was recorded using the same fused silica Dewar assembly and immersion of the samples in liquid nitrogen.

The up-conversion fluorescence spectra were measured with Acton SP-2500i spectrograph at room ($T_R = 298$ K) and liquid nitrogen ($T_{LN} = 77$ K) temperatures using a Ti-sapphire 800 nm fs laser, Mira Optima 900-F, for excitation. Recorded emission spectra were corrected for the grating efficiency, CCD spectral sensitivity and transmittance of the colored glass filter, used for elimination of the scattered 800 nm light.

3. Results and discussion

Optical transmission spectra of Er-doped CsCl-Ga-Ge-S glasses at room and LN temperatures are shown in Fig. 1. The same spectra of undoped glass (insert to Fig. 1) looked featureless in good agreement with other studies [8], which allowed the assignment of the observed absorption bands in Fig. 1 explicitly to the absorption of Er in CsCl-Ga-Ge-S glass matrix. The absorption lines observed at room temperature located at ~491, ~524, ~546, ~658, ~803 and ~981 nm correspond to known Er^{3+} ion transitions identified as $^4I_{15/2} \rightarrow ^4F_{7/2}$, $^4I_{15/2} \rightarrow ^2H_{11/2}$, $^4I_{15/2} \rightarrow ^2S_{3/2}$, $^4I_{15/2} \rightarrow ^4F_{9/2}$, $^4I_{15/2} \rightarrow ^4I_{9/2}$ and $^4I_{15/2} \rightarrow ^4I_{11/2}$, respectively [10,12–15]. The strongest absorption appears at ~524 nm (Fig. 1). The temperature decrease leads to a significant (~30 nm) short-wave shift of the fundamental optical absorption edge for all of the investigated glasses (Fig. 1), which is consistent with known temperature behavior of the optical gap for this class of amorphous materials [16]. All the above absorption lines are observed at LN temperature too; their positions are about the same, but the intensity slightly increases (Fig. 1). At the same time, at LN temperature, an additional absorption band at ~453 nm, not present in room temperature transmission spectra, becomes noticeable. This absorption corresponds to $^4I_{15/2} \rightarrow ^4F_{3/2}$ transition of Er^{3+} ion [12–15] and has never been observed in chalcogenide matrixes due to its overlap with fundamental optical absorption edge of previously studied compositions. The transition, however, has a significant impact on fluorescence spectra, as can be ascertained from Fig. 2. The observed absorption and emission lines are summarized more concisely in energy level diagram in Fig. 3.

The fluorescent spectra of un-doped and Er-doped CsCl-Ga-Ge-S glasses at room and LN temperatures are shown in Fig. 2. As expected, the un-doped samples do not show any fluorescence neither at room or LN temperatures (Fig. 2a and b). When 0.6 or 1.0% of Er is introduced into the matrix, the room-temperature

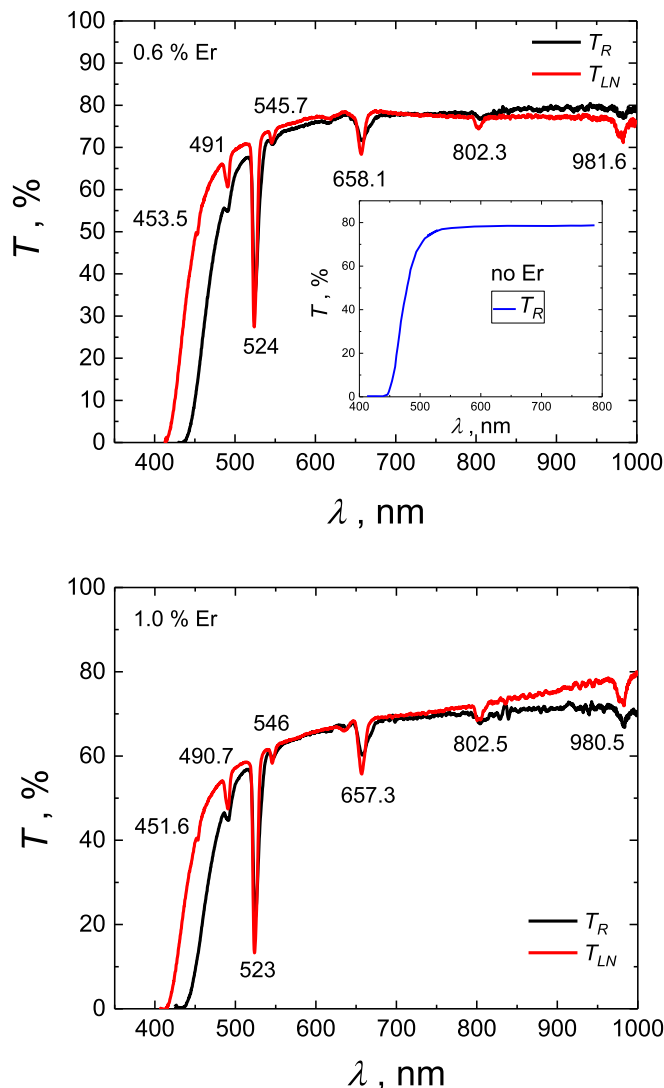


Fig. 1. Transmission spectra of 65GeS₂-25Ga₂S₃-10CsCl glasses un-doped (insert) and doped (main figures) with 0.6 and 1.0 at.% of Er, recorded at room (T_R) and liquid nitrogen (T_{LN}) temperatures. Indicated wavelengths correspond to Er^{3+} ions absorption.

fluorescence shows four distinct emission features in 900–1650 nm range, namely bands at ~990, ~1170, ~1250 and ~1550 nm (Fig. 2c,e). The origin of these bands can be understood from the analysis of energy level diagram for Er^{3+} ions in Fig. 3 and excitation spectrum in Fig. 2. From this data, it follows that the excitation wavelengths at which the fluorescence is observed directly correspond to the absorption lines observed in transmission spectra of the investigated Er-doped CsCl-Ga-Ge-S glasses (Fig. 1). Absorbing ~800 nm wavelength light would populate the $^4I_{9/2}$ level of the Er^{3+} ion, which may decay via a multiphonon relaxation mechanism [12] and populate the $^4I_{11/2}$ and $^4I_{13/2}$ levels, resulting in the observed emission at ~990 and 1550 nm (Fig. 2c, e) due to the ground state $^4I_{11/2} \rightarrow ^4I_{15/2}$ and $^4I_{13/2} \rightarrow ^4I_{15/2}$ radiative transitions (Fig. 3). The excitation from ~660 nm wavelength light leads to a population of $^4F_{9/2}$ level, which may directly result in the $^4F_{9/2} \rightarrow ^4I_{13/2}$ radiative transition responsible for the observed emission band at ~1170 nm (Fig. 2c,e), or decay into $^4I_{9/2}$ or $^4I_{11/2}$ states radiatively or non-radiatively. The following ground state $^4I_{11/2} \rightarrow ^4I_{15/2}$ and $^4I_{13/2} \rightarrow ^4I_{15/2}$ radiative transitions would also contribute to the emission at ~990 and ~1550 nm (Fig. 2c, e). The excitation with ~490, ~530 and ~550 nm wavelengths results in a

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