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Design of rare-earth-ion doped chalcogenide photonic crystals for enhancing the fluorescence emission

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ABSTRACT

Rare-earth-ion doped chalcogenide glass is a promising material for developing mid-infrared light sources. In this work, Tm^{3+} -doped chalcogenide glass was prepared and photonic crystal structures were designed to enhance its fluorescence emission at approximately $3.8 \mu\text{m}$. By employing the finite-difference time-domain (FDTD) simulation, the emission characteristics of the luminescent centers in the bulk material and in the photonic crystals were worked out. Utilizing analysis of the photon excitation inside the sample and the photon extraction on the sample surface, it was found that fluorescence emission can be significantly enhanced 260-fold with the designed photonic crystal structure. The results of this work can be used to realize high-efficiency mid-infrared light sources.

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1. Introduction

Mid-infrared (Mid-IR) light sources are among the most extensively developed photonic devices in recent years. Their spectral ranges encompass the important atmospheric transmission windows of $3\text{--}5 \mu\text{m}$ and $8\text{--}12 \mu\text{m}$, covering the molecular fingerprints of numerous gases, liquids and solids. Therefore, mid-IR light sources can be used in many important practical applications, such as biomedical sensing, environmental monitoring, manufacturing processes, and quality control [1–5].

Rare-earth-ion (REI) doped chalcogenide glasses and fibers are interesting materials for developing mid-IR sources [6,7]. As hosts for REIs, the low phonon energy of chalcogenide glasses allow the activation of many mid-IR and long IR REI transitions that are usually quenched in silica and fluoride glasses [8]. Among various REIs, trivalent thulium (Tm^{3+}) ions have received considerable attention recently, due largely to the fact that their emission spectra include wavelengths from the near-IR (NIR) to mid-IR spectrum. Also, the absorption band of the $^3\text{H}_4$ state of Tm^{3+} ions at $0.8 \mu\text{m}$ facilitates the use of commercial GaAlAs diode lasers as pump sources [9]. Spectroscopic studies [3,6] and modeling [10] of REI doped chalcogenide glasses have demonstrated that they are a suitable medium to achieve lasing activities in the $3\text{--}5 \mu\text{m}$ wavelength range. However, the lasing activity is still limited in the NIR region and not available in the mid-IR region, with even the

fluorescence emission in the latter being very weak. Therefore, effective approaches are needed to enhance the mid-IR fluorescence emissions of REI-doped chalcogenide glasses.

Controlling the chemical environment of REIs through crystallization is one of the most efficient ways to enhance the fluorescence efficiency. In fact, enhanced fluorescence has already been obtained in REI-doped chalcogenide glass-ceramics [11–13]. However, research on the mid-IR transitions of REIs is scarce, and the fundamental mechanism of the enhancement of the mid-IR fluorescence emission upon crystallization still remains largely unknown.

Building photonic crystal (PC) structures is a promising approach to developing efficient mid-IR light sources [14–16]. PCs are periodic dielectric materials exhibiting photonic band gaps (PBGs), where light of certain energies cannot propagate [14]. Although PCs were first proposed to inhibit spontaneous emissions of luminescent materials, the following research has demonstrated their ability to precisely control the radiation and propagation of photons. The enhancement of the emission and directionality by PCs rapidly attracted the interest of many researchers, leading to the development of low threshold PC lasers [17]. PCs have shown a great potential for photon control in the visible and the NIR spectra [18,19]. However, studies of the fluorescence enhancement in the mid-IR region have rarely been reported.

In this work, Tm^{3+} -doped chalcogenide glass was fabricated and its spectral characteristics were experimentally studied. Tm^{3+} ions were selected as a dopant due to their fluorescence emission peak of approximately $3.8 \mu\text{m}$ [9], which coincides with an atmospheric transmission window for potential applications. With the

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measured optical parameters of the Tm^{3+} -doped chalcogenide glass, uniform PCs and PCs with cavity arrays were proposed to enhance the fluorescence emission. The density of optical states (DOS) of the sample and the emission efficiency from the sample surface were calculated using FDTD simulation tools [20,21]. Our results demonstrate that this photonic crystal can significantly enhance the excitation of Tm^{3+} and improve the coupling of the fluorescent emissions into air. Thanks to the contribution of the designed 2D PCs, the mid-IR fluorescence emissions can be enhanced, regardless of whether the emission center is within or on the edge of the band gap. Utilizing the resonance of the PC cavity arrays, the fluorescence emission in Tm^{3+} doped chalcogenide glasses can be enhanced more than 260 times.

2. Theory

When externally incident light interacts with periodically modulated structures (as with PCs), in addition to the original incident direction, higher order diffractive beams will be allowed to propagate into the sample. This will in turn reduce the reflected energy so as to increase the intensity of the excitation light, a factor that cannot be ignored for samples with high refractive index. This effect will also occur when the emitted fluorescence escapes from the sample into the air. Like directional emissions, the fluorescence can now move out of the structure by Bragg scattering, thereby greatly reducing the amount of light trapped through total internal reflection compared with an unpatterned substrate. It can thus be appreciated that an enhancement of fluorescence can be achieved in two steps: enhanced excitation and enhanced extraction.

It is well known that the excitation efficiency of luminescent centers embedded within the sample is proportional to the density of optical states (DOS), which is defined as [22]

$$N(\omega) = \sum_{\mathbf{n}} \int_{1, \text{BZ}} d^3\mathbf{k} \delta(\omega - \omega_{\mathbf{n}\mathbf{k}}), \quad (1)$$

with the integration over the whole first Brillion Zone (BZ), where $\omega_{\mathbf{n}\mathbf{k}}$ are the eigen-frequencies of the electric field modes with vector \mathbf{k} and band index \mathbf{n} . The DOS highly depends on the structure of the sample, thus opening a path to engineer the fluorescence emission by structural design.

Due to the fact that we are only concerned with the fluorescence emission from the top surface of the sample, it is required to carry out coupling simulations of the fluorescence emission at the interface with the modulated structures. This can be done through the vector analysis explained as follows: the component of the wave vector of the emitting photon in air can be expressed as [23]: $k = \omega/c(\cos\theta, \sin\theta)$, where θ is the angle with respect to normal direction. It is worth noting that the exiting angle θ of light differs from the light propagation angle inside the PC [24], while the latter depends on the effective refractive index and the presence of additional propagating modes when diffraction inside the material occurs. When the allowed photon mode in the first BZ was calculated, the fluorescence emission that has escaped from the sample surface can be obtained by two conservation laws: (i) parallel momentum conservation, and (ii) energy conservation. These two conditions can be written for PCs as [25]

$$\begin{aligned} \mathbf{k}_{//} + \mathbf{G}_{//} &= \frac{\omega}{c} \sin \theta, \\ \epsilon_{\mathbf{n}}(\mathbf{k}_{//}, \mathbf{k}_z) &= \hbar\omega, \end{aligned} \quad (2)$$

where $\mathbf{k}_{//}$ and \mathbf{k}_z are the components of \mathbf{k} parallel and perpendicular to the surface, respectively; $\mathbf{G}_{//}$ is the parallel component of any reciprocal lattice vector \mathbf{G} ; and $\epsilon_{\mathbf{n}}(\mathbf{k}_{//}, \mathbf{k}_z)$ is the \mathbf{n} th order energy band of the photon with momentum \mathbf{k} . Many more photon modes will be extracted due to the contribution of the lattice

vector \mathbf{G} , thereby leading to a significant enhancement of the fluorescence emission.

The DOS of the escaped fluorescence emission was then calculated by summing over these selected field modes

$$N(\hbar\omega) = \sum_{\mathbf{n}, \mathbf{k}_z \geq 0} \delta[\epsilon_{\mathbf{n}}(\mathbf{k}_{//}, \mathbf{k}_z) - \hbar\omega] \quad (3)$$

where $\mathbf{k}_{//}$ is defined by Eq. (2). The $N(\hbar\omega)$ is summed only over $\mathbf{k}_z \geq 0$, while for the direction $\mathbf{k}_z < 0$, the propagation is attenuated. The calculations were performed with the step $\Delta\omega = 10^{-3} \bullet 2\pi c/\Lambda$ considering the accuracy and the computer time. The numerical accuracy was tested with the PC structure data given in [23], and the validity of the numerical simulation was proven.

3. Experimental and simulation results

3.1. Glass preparation and spectroscopic testing

Pure-sulfur based glasses were developed by introducing the element gallium (Ga), due to the fact that Ga-containing chalcogenide glass is recognized as a superior host for REIs and is regarded as relevant to mid-IR lasers. Iodine and selenium were also introduced in order to improve their resistances towards crystallization. The best compromise has been obtained with the 72GeS₂–18Ga₂S₃–10CsI (GGSI) (in mol%) composition.

Bulk glass with the composition of 72GeS₂–18Ga₂S₃–10CsI doped with 1 wt% Tm^{3+} was prepared by the melt-quenching method. High purity elements (Ge, Ga, and S of 5-N purity, CsI of 3-N purity) and Tm_2S_3 (3-N purity, Aldrich) were used as the starting materials and were well grounded. The powders were weighed and filled into silica ampoules by a glove box full of Ar gas to avoid contamination from oxygen and moisture. Then, the ampoules were sealed while being continuously evacuated. The starting powders were melted using a rocking furnace at 950 °C for 10 h and finally quenched in ice water. Subsequently, the obtained glass sample was annealed at a temperature slightly below the glass transition temperature ($T_g - 10$ °C) before being slowly cooled down to room temperature.

All optical tests were carried out at room temperature. In order to measure the refractive indexes, the glasses were cut into disks of 2 mm in thickness. The refractive indexes were determined from the single surface reflection coefficient according to [26]

$$\frac{n(\lambda)}{n_{\text{air}}} = \frac{1 + \sqrt{R(\lambda)}}{1 - \sqrt{R(\lambda)}} \quad (1')$$

where $n_{\text{air}} = 1.0003 \pm 0.0003$. The measurements in the IR range beyond 2 μm were performed with a Nicolet 5700 FTIR spectrophotometer. Reflectance measurements were performed with a specular reflectance accessory that was placed in the sample beam with an incident angle of 10°. Infrared transmissions were also measured with the Nicolet 5700 FTIR-spectrophotometer by removing the reflectance accessory. The good transmission property provided a high optical quality of the prepared sample.

The absorption spectra were recorded in the range of 400–3000 nm with a Perkin-Elmer Lambda 950 UV–VIS–NIR spectrophotometer. A Ti: Sapphire laser (Coherent Mira 900-D) at 800 nm was used as the excitation source in order to obtain efficient fluorescence emission. The mid-IR fluorescence spectra in the range of 2000–4100 nm were measured through a computer-controlled system that consisted of a Zolix Omni- λ 3015 monochromator with a SCITEC Model420 lock-in amplifier and an InSb detector (DInSb 55-De) cooled with liquid nitrogen.

Fig. 1(a) shows absorption spectra of glasses doped with 1.0 wt % Tm^{3+} . The optical absorption bands are assigned according to

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