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Broadband mid-infrared emission around 2.9 μm in Dy^{3+} doped bismuth germanate glass

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ABSTRACT

Bismuth germanate glasses doped with a series of different concentrations of trivalent dysprosium ions were synthesized using melt-quenching method. The complex glass network is characterized by Raman spectrum, to put in evidence a structure combining [BiO_3] pyramidal units, [BiO_6] octahedral units and [GeO_4] tetrahedral units. The arrangement of these structural units attract the introduction of Dy^{3+} ions thanks and endow the bismuth glass with the efficiently broadband mid-infrared emission. Upon the excitation source of an 808 nm laser diode, a flat and broad emission from 2.5 μm to 3.2 μm with a bandwidth of 374 nm was obtained in a 1.0mol% Dy_2O_3 doped glass, which corresponds to $^6H_{13/2} \rightarrow {}^6H_{15/2}$ transition. The emission cross section around 2.9 μm is estimated to be 7.78×10^{-21}cm^2 based on the fluorescence spectrum. Hence, the advantageous spectroscopic characteristics reveal that Dy^{3+} doped bismuth gernamate glass is a potential cost effective host for the mid-infrared solid state lasers.

1. Introduction

Electronic transitions between several energy levels in rare earth (RE^{3+}) are capable of yielding mid-infrared luminescence. To date, among all the lanthanide ions, Er^{3+}, Pr^{3+}, Nd^{3+}, Ho^{3+} and Dy^{3+} doped matrix have been investigated extensively in literature [1–5]. The low-phonon energy crystals (e.g., $LaCl_3$ [6], KPb_2Cl_5 [7]) and low-phonon glass (e.g., ZBLAN [8], ZBLAY [9], chalcogenide [10,11]) are attractive as these ions doped hosts for mid-infrared laser applications because of the small energy gaps between the involved and intermediate states of the RE^{3+} ions. Their lower lattice vibrations are beneficial to avoid non-radiative relaxation of the excited states [11].

Owning to the $^6H_{13/2} \rightarrow {}^6H_{15/2}$ transition, Dy^{3+} is a natural candidate for 3 μm laser output. A laser action around 3 μm has been reported from Dy^{3+} doped BaY_2F_8 host crystal [12]. The fluoride and chalcogenide glass as promising hosts have been extensively adopted for Dy^{3+} doping to realize the more mid-infrared emission intensity. It has been indicated that the quasi-continuous wave output at 2.96 μm from a Dy^{3+}-doped ZBLAN fiber is pumped by a ~1.3 μm Nd:YAG laser [13]. The detailed spectroscopic properties and host dependence of Dy^{3+}, Dy^{3+}/Tm^{3+}-doped chalcogenide glass pumper by 808 nm LD have been reported [14].

To further exploit the potential hosts for Dy^{3+} doping, many other glass system (tellurite [15], germinate [15], fluorophosphates [13]) were prepared and studied, but little effort was put on the bismuth glass. Bismuth germanate glass is characterized by high refractive index (2.1), good mid-IR transmission property and significantly low phonon energy (440 cm^{-1}) [16]. These outstanding properties will enhance the Dy^{3+}:$^6H_{13/2} \rightarrow {}^6H_{15/2}$ transition. In current work, we prepared a series of Dy^{3+}-doped bismuth germanate glass of varying Dy^{3+} concentration by melt-quenching method. The absorption spectra were tested and spontaneous transition probability, stimulated emission cross section are estimated and discussed. The luminescent spectra were obtained pumped by 808 nm LD and the related energy transfer mechanism is demonstrated.

2. Experimental

The investigated glasses have the following compositions in cation%: $55BiO_{1.5}$-$30GeO_2$-$15NaO_{0.5}$-xDy_2O_3 (x = 0, 0.1, 0.4, 0.7, 1.0, and 1.2, named as BGD0, BGD0.1, BGD0.4, BGD0.7, BGD1.0, BGD1.2,

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respectively). The raw materials were prepared from high-purity Bi_2O_3, GeO_2, Na_2CO_3 and Dy_2O_3 powder. Well-mixed raw materials (30 g) were placed in alumina crucible and melted at 1050 °C for 30 min in oxygen atmosphere. Bubbling dry oxygen gas in melt was used to minimize the hydroxyl groups. The melts were quickly poured on preheated stainless-steel mold and annealed for 2 h near the glass transition temperature (T_g). The annealed sample was fabricated and polished to the size of $20 \times 10 \times 1\ mm^3$ for optical property measurements.

Refractive indices were detected at room temperature using a Metricon Model 2010/M Prism Coupler. The mid-infrared transmission spectrum was obtained by using a Thermo Nicolet (Nexus FT-IR spectrometer) in the range of 2.5–10 μm. The Raman spectra of the glasses were measured with a Renishaw InVia Raman spectrophotometer using the 488 nm excitation line from a spectra physics laser. The absorption spectra were recorded with a Perkin-Elmer Lambda 900UV/VIS/NIR spectrophotometer with 1 nm step. The fluorescence spectra were measured by TRIAX550 spectrophotometer with 808 nm LD as excitation source. All the measurements were done at room temperature.

3. Results and discussion

3.1. FTIR transmission spectra and Raman spectra

The FTIR transmission spectra (Fig. 1) of prepared glass samples (1 mm thickness) are recorded within the wavelength region from 2.5 μm to 7 μm. In the figure, the maximum transmittance reaches 78% due to the heavy mass of Bi ions. The typical absorption band around 3 μm is attributed to OH^- group [17]. However, the maximum transmittance becomes low as the increasing Dy^{3+} content. It is indicated that Dy^{3+} ions have a severely absorption band around 3.0 μm [18]. Meanwhile, the intense absorption of Dy^{3+} ions make increasingly contribution to 3 μm absorption band. Therefore, the hydroxyl group concentration should been calculated in Dy^{3+} ions free glass. The OH^- content can be expressed by the absorption coefficient around 3 μm owning to hydroxyl molecule vibrational mode [19]:

$$\alpha_{OH^-} = \ln(T/T_0)/l \quad (1)$$

where l depicted the thickness of sample, T and T_0 are the transmitted and incident intensities, respectively. The calculated α_{OH^-} of BGD0 sample is 0.64 cm^{-1}, which is lower than the optimum absorption coefficient (2 cm^{-1}) for excellent laser performance [20].

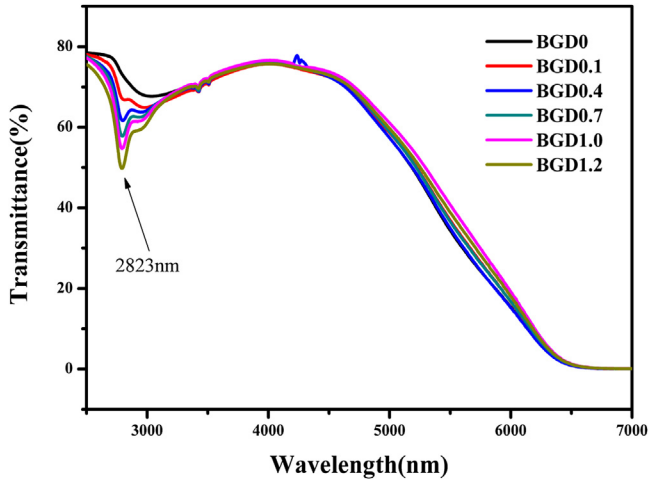

Fig. 1. Mid-infrared transmission spectra of Dy^{3+} doped bismuth germanate glasses (1 mm thickness).

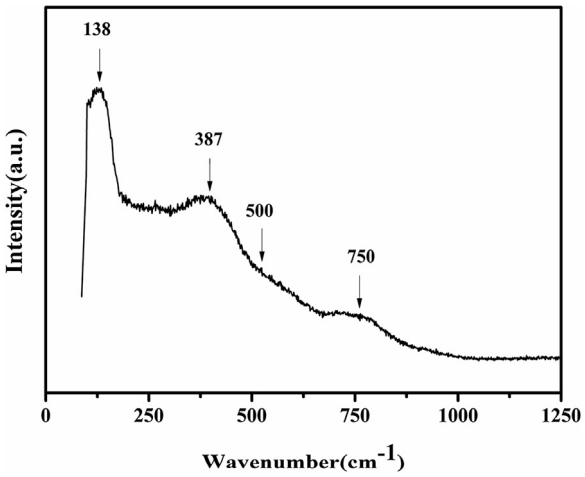

Fig. 2. Raman spectrum of BGD0 sample.

Raman spectrum of BGD0 sample is depicted in Fig. 2, which is in terms of the vibrational modes of glass network units used to evaluate the structural information of bismuth germanate glass. As shown in Fig. 2, three prominent and broad bands are observed in the region from 100 cm^{-1} to 1250 cm^{-1}. The most intense band centered at 138 cm^{-1} is assigned to the vibration of Bi^{3+} in structural units [21]. The second intense and broad band at 387 cm^{-1} is assigned to Bi-O-Bi symmetric stretching of [BiO_3] pyramidal units and [BiO_6] octahedral units [22,23], overlapping with the peak shoulder at 500 cm^{-1} caused by Ge-O-Ge symmetric stretching of [GeO_4] tetrahedral units [24,25]. The single peak at 750 cm^{-1} is attributed to the motion of Ge-O^- involving two non-bridged oxygen atoms of [GeO_4] tetrahedral units [21]. The bismuth germanate glass network are mainly composed of [BiO_3] pyramidal units, [BiO_6] octahedral units and [GeO_4] tetrahedral units. The two glass former, Bi_2O_3 and GeO_2, produces the complex network structure, providing an abundant of sites for broadening emission of Re^{3+} ions. In the case of bismuth germanate glass, the low phonon energy will be beneficial to the reduction of non-relaxation of emitting level.

3.2. Absorption spectra and Judd-Ofelt analysis

Fig. 3 shows the optical absorption spectra of bismuth germanate glasses with the different Dy^{3+} concentration. Due to the intrinsic absorption edge at the short wavelength side at 450 nm of the host glass, the absorption bands of energy levels higher than $^4I_{15/2}$ are not observed. Totally the absorption bands are observed at 454 nm, 473 nm, 753 nm, 801 nm, 896 nm, 1094 nm, 1271 nm and 1675 nm, which are assigned to the transitions from the ground state $^6H_{15/2}$ to the higher states $^4I_{15/2}$, $^4F_{9/2}$, $^6F_{3/2}$, $^6F_{5/2}$, $^6F_{7/2}$, $^6H_{7/2} + {}^6F_{9/2}$, $^6H_{9/2} + {}^6F_{11/2}$ and $^6H_{11/2}$, respectively. By comparison, there is no wavelength shift and no obvious change in the shape in absorption band corresponding to each transition of samples. And the absorption intensity increases linearly with the Dy^{3+} concentration. This shows the uniform local ligand sites around Dy^{3+} in glass network. The evidently absorption band centered at 801 nm indicates that these samples can be efficiently pumped by 808 nm laser diode.

Using the Judd–Ofelt theory, the radiative parameters of the excited states of Dy^{3+} in bismuth glass are estimated [26,27]. The spontaneous transition probability (A), branching ratio (β) and radiative lifetime (τ) of various transitions in BGD1.0 samples are shown in Table 1. The theory and detailed calculated procedure