Solid State Sciences 31 (2014) 54–61

Contents lists available at ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie

Structure and spectroscopic properties of Er^{3+} doped germanate glass for mid-infrared application

Tao Wei [a], Fangze Chen [a], Xufeng Jing [b], Fengchao Wang [a], Ying Tian [a],*, Shiqing Xu [a],*

[a] College of Materials Science and Engineering, China Jiliang University, Hangzhou 310018, PR China
[b] Institute of Optoelectronic Technology, China Jiliang University, Hangzhou 310018, PR China

ARTICLE INFO

Article history:
Received 8 January 2014
Received in revised form
22 February 2014
Accepted 24 February 2014
Available online 6 March 2014

Keywords:
Er^{3+} doped germanate glass
Mid-infrared properties
Glass structure
Gain coefficient
Stark splitting

ABSTRACT

Intense 2.7 μm emission derived from modified Er^{3+} doped germanate glass was reported. Raman spectrum analysis was carried out to grasp glass structure. Based on the absorption spectrum, the Judd–Ofelt parameters and radiative properties were calculated originated from Judd–Ofelt theory. 2.7 μm emission characteristics, stark splitting features and energy transfer processes upon excitation of a conventional 808 nm or 980 nm laser diode were carefully investigated. The prepared glass possesses high spontaneous transition probability (34.28 s^{-1}), large calculated emission cross section (13×10^{-21} cm^2) and gain coefficient (5.4 cm^{-1}) for the $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition. These results indicate that Er^{3+} doped germanate glass has potential applications in mid-infrared lasers and amplifiers.

1. Introduction

In recent years, rare earth doped mid-infrared (MIR) fiber laser has been paid considerable attention by researchers because of their wide applications in laser radar, remote sensing, medical surgery, military countermeasures and atmosphere pollution monitoring [1–7]. So far, ~3 μm fiber laser with high efficiency has been demonstrated in Er^{3+}, Ho^{3+} and Dy^{3+}, etc. [4,7,8]. It is reported that ~3 μm emissions from Ho^{3+} and Dy^{3+} doped fiber laser have been achieved via the excitation of Nd:YAG laser or Yb^{3+} doped silica fiber laser [4,6,7]. However, the realization of ~3 μm emissions of Ho^{3+} and Dy^{3+} ions requires complex pump arrangements owing to no overlap between their ground-state absorption transitions and the emissions from commonly high-power diode lasers. In comparison to Ho^{3+} and Dy^{3+} ions, 2.7 μm emission corresponding to Er^{3+}:$^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition can be pumped more easily by traditionally 808 nm or 980 nm laser diode. Due to the popularity of Yb^{3+} fiber laser and Nd crystal laser, the technology of 980 nm and 808 nm laser diodes have been developed greatly and got more mature. Moreover, due to their merits of low-cost, high reliability and stability, both 808 nm and 980 nm diode lasers are good pumping laser sources for Er^{3+} ions [8,9]. For Yb^{3+} fiber laser, 980 nm LD is a suitable pump source while 808 nm LD is a much better pump source for Nd^{3+} laser.

In order to improve MIR emission performance, choosing an appropriate glass matrix is required. Last decades have witnessed the great development of fluoride, tellurite, bismuth and germanate glasses for mid-infrared applications [10–13]. Among those mentioned above, germanate glass has been regarded as a promising host for MIR application due to its combination of low phonon energy, high transmittance in a wide wavelength region, good glass forming ability, superior thermal stability and chemical durability [14–16]. In particular, Barium gallogermanate (BGG) glass is an excellent candidate for optical applications, since BGG is a stable oxide glass, and its fabrication process is relatively simple. Besides, BGG system is scalable to significantly larger size [17].

However, BGG glass has the disadvantage of high melting temperature and amounts of hydroxyl groups. In order to compensate these defects, fluoride can be added to BGG glass to reduce OH^- group concentration through a reaction $OH^- + F^- \rightarrow O^{2-} + HF\uparrow$, and to further minimize the maximum phonon energy. Thus, 2.7 μm emission property is expected to be enhanced [14,18]. On the other hand, introduction of fluoride can lower the melting temperature, which is advantageous for energy conservation [19]. In addition, it has been proven that the properties of BGG glass can also be

---

* Corresponding authors. Tel.: +86 571 8683 5781; fax: +86 571 2888 9527.
E-mail addresses: weitao0916@sina.com (T. Wei), tianyingcjlu@163.com, tianying0204@163.com (Y. Tian), sxucjlu@hotmail.com (S. Xu).

http://dx.doi.org/10.1016/j.solidstatesciences.2014.02.019
1293-2558/

modified by adding other components, such as Y_2O_3 and La_2O_3 [20]. Also, BaF_2 and NaF are introduced to modify glass forming ability.

As far as we know, Er^{3+} ions are capable of absorbing 808 nm and 980 nm pumping light via the $^4I_{15/2} \rightarrow {}^4I_{9/2}$ and $^4I_{15/2} \rightarrow {}^4I_{11/2}$ transitions. But to the best of our knowledge, very few reports on 2.7 μm fluorescence properties especially stark splitting features in Er^{3+} doped germanate glass pumped by 808 nm and 980 nm LD have been carried out. The present work investigated the mid-infrared emission properties of Er^{3+} doped germanate glass excited by 808 nm and 980 nm LD. The emission bandwidth, stimulated absorption and emission cross sections as well as gain spectra have been discussed. Corresponding energy transfer process in Er^{3+} doped germanate glass has also been analyzed. A combination discussion of absorption data and the Judd–Ofelt analysis was performed. Moreover, Raman spectrum was investigated to take knowledge of glass structure origin.

2. Experimental details

Er^{3+} doped germanate glass was prepared by traditional melting and quenching method, which has the compositions of $65GeO_2$–$12Ga_2O_3$–$3BaO$–$5BaF_2$–$5NaF$–$5La_2O_3$–$5Y_2O_3$–$1Er_2O_3$ in mol%. Powders of high-purity GeO_2, Ga_2O_3, BaO, BaF_2, La_2O_3, Y_2O_3, NaF, and Er_2O_3 were used as raw materials. Well-mixed 10 g batches of the sample was placed in a high-purity alumina crucible and melted in a Si–Mo resistance furnace at 1400 °C for 30 min. Then quenched on preheated stainless steel plate and annealed at about 500 °C for 6 h before they were cooled to room temperature. The annealed sample was finally cut and optically polished to the size of 20 mm × 10 mm × 1.5 mm for the optical property measurement.

The density of the sample was conducted via the Archimedes principle using distilled water as the immersion medium with maximum error of ±2% whereas the refractive index of 1053 nm was recorded by the prism minimum deviation method with error limit of ±0.05%. The measured density and refractive index are 4.70 g/cm^3 and 1.72, correspondingly. The thermal analysis was performed by differential scanning calorimeter (DSC) at the heating rate of 10 K/min with maximum error of ±5 °C. The characteristic temperatures such as temperatures of glass transition T_g, onset crystalline T_x and top crystalline peak T_p were determined by doing tangent nearby the characteristic points. The structure of glass was analyzed using Raman spectrum, which was measured with an FT Raman spectrophotometer (Nicolet MODULE) in the spectral range of 100–1600 cm^{-1}. The absorption spectrum was undergone by means of a Perkin Elmer Lambda 900UV–VIS–NIR spectrophotometer in the range of 350–1640 nm with a resolution of 4 cm^{-1}. The emission spectra in the range of 1400–1700 nm and 2600–2800 nm were obtained with a computer-controlled Triax 320 type spectrometer upon excitation of an 808 nm laser diode (LD) and a 980 nm LD. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Thermal stability

The DSC curve of present sample is determined for temperatures of glass transition T_g, onset crystallization T_x, and top crystallization peak T_p, which is shown in Fig. 1. It is evidently observed that the studied sample possesses higher T_g (652 °C) compared with tellurite (~400 °C) [21], bismuth (370 °C) [22] and other germanate (611 °C) [23] glasses. It is well known that the high T_g is capable of resisting thermal damage at high pumping intensities [10]. Furthermore, the ΔT ($T_x - T_g$) has been frequently used as a rough estimate of glass stability against crystallization [10]. The ΔT of prepared sample can reach to 136 °C, which is much larger than those of ZBYA (89 °C) and ZBLAN (82 °C) [10], indicating that the investigated glass has better thermal stability against crystallization.

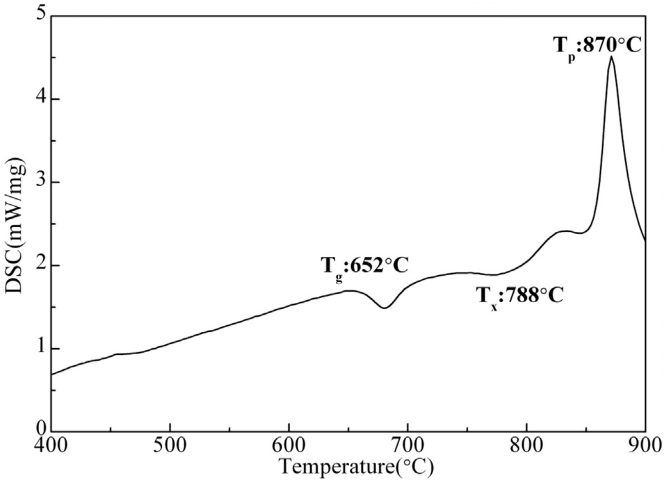

Fig. 1. DSC curve of germanate glass host.

3.2. Raman spectrum analysis

In order to comprehend the structure of prepared glass, Raman spectrum analysis is performed as displayed in Fig. 2. Eight symmetric vibrational modes of the glass are obtained by Gauss fitting technique. These peaks are also assigned in Fig. 2 according to the reports of other germanate glasses containing modifying oxides and GeO_2 quartz [24]. Features in the Raman spectrum can be grouped into three frequency ranges: low frequency region below 300 cm^{-1}, intermediate frequency region (300–600 cm^{-1}) and high frequency region above 600 cm^{-1} [25]. The Raman peaks at low wavenumber A and B, centered at 118 cm^{-1} and 243 cm^{-1}, respectively, represent the vibration of network-modifying cations in large interstitial sites. Intermediate frequency regions are dominated by a peak C, centered at 487 cm^{-1} that has been assigned to various Ge–O–Ge bending vibrational modes. The high energy Raman peaks D, E, F, G, H, peaked at 876 cm^{-1}, 887 cm^{-1}, 939 cm^{-1}, 1066 cm^{-1} and 1104 cm^{-1}, contribute to the stretching mode of Ge–O and Ga–O structure units in the environment of

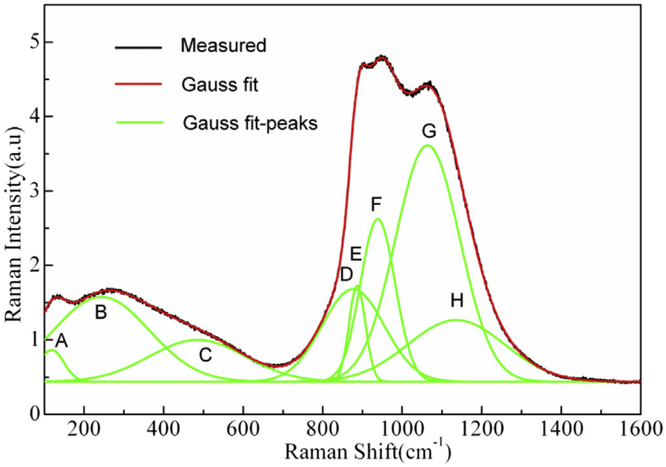

Fig. 2. Raman spectrum of Er^{3+} doped germanate glass.