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Comprehensive evaluation of the structural, absorption, energy transfer, luminescent properties and near-infrared applications of the neodymium doped germanate glass

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ABSTRACT

Nd^{3+} doped germanate glass with good thermal stability was investigated through absorption, near-infrared emission spectrum and lifetime measurement. Intensity parameters ($\Omega_{2,4,6}$) and spectroscopic quality factor ($\chi = \Omega_4/\Omega_6$) were analyzed in detail on the basis of the Judd–Ofelt theory. The calculations of bonding parameters and the degree of ionic or covalent bonding character demonstrate the nature of ionic bonding of the prepared sample. It is found that the present glass possesses large spectroscopic quality factor of 93%, high stimulated emission cross section, fluorescence branching ratio and optical gain parameters as well as lower saturation intensity at 1.05 μm. Thus, the excellent radiative properties owing to $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition reveal the favorable laser action at 1.05 μm. Nd^{3+} doped germanate glass might have potential advantages for near-infrared applications.

1. Introduction

Solid state laser with high power operating at 1.05 μm wavelength has recently attracted much attention because of its potential applications such as photonic devices for high-density optical storage, optoelectronics, and medical diagnostics as well as optical communication systems [1–4]. Nd^{3+} doped glasses have been investigated widely for the 0.9, 1.05 and 1.33 μm lasers due to the transitions of $^4F_{3/2} \rightarrow {}^4I_{9/2,11/2,13/2}$ for scientific, industrial and telecommunication fields [5]. The choice of Nd^{3+} ion is due to its prominent features including many excited levels suitable for optical pumping, sharp absorption and emission bands from ultra violet (UV) to infrared (IR) spectral range and longer fluorescence lifetimes [6]. Moreover, a commercially available 808 nm laser diode can be used to excite Nd^{3+} ion for 1.05 μm emission. Owing to the commercial importance of Nd^{3+} doped glasses, many studies on optical and spectroscopic properties of Nd^{3+} in the various glass matrixes have been carried out [2,5,7,8]. It is well known that optical and spectroscopic properties of Nd^{3+} ions to a large extent depend on the chemical composition of glass host [9]. By the optimal choice of network former and modifier, high 1.05 μm emission efficiency can be achieved from Nd^{3+} ions. A suitable glass system that has an advantageous ligand field environment might have a positive influence on spectroscopic properties such as the optical absorption cross section, stimulated emission cross section, fluorescence decay and the quantum efficiency of Nd^{3+} ions [1].

Among all kinds of glasses, germanate glass combines the merits of moderate maximum phonon energy (800–900 cm^{-1}), wide infrared transmittance (~6.5 μm) and high refractive index, which is beneficial for minimizing multi-phonon relaxation rate and increasing quantum efficiency of the excited states of Nd^{3+} ions [10]. However, traditional Nd^{3+} doped germanate glass has the disadvantages of high melting temperature, high viscosity and a large amount of hydroxyl groups that may cause fluorescence quenching because of the unexpected energy transfer between Nd^{3+} and OH^- ions [13]. Based on this idea, the 1.05 μm emission has been reported in lead–niobium–germanate glass doped Nd^{3+} ions [11]. Unfortunately, the toxic component of PbO in germanate glass is not environmentally friendly. Hence, a new type of environmentally friendly Nd^{3+} doped germanate glass is desirable for various applications. Barium gallogermanate glass is an excellent optical material for infrared window application [12]. It is reported that the substitutions of BaF_2 for BaO can greatly minimize the OH^- concentration and enhance emission intensity via efficient energy transfer of rare earth ions [13,14]. Furthermore, it has been

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demonstrated that the properties of germanate glass can be modified by adding other components, such as La_2O_3 and Li_2O [15,16].

In the present work, the germanate glass with molar compositions of $65GeO_2$–$8Ga_2O_3$–$17BaF_2$–$5La_2O_3$–$5Li_2O$–$1Nd_2O_3$ has been prepared by melt-quenching technique. We have investigated the spectroscopic properties of Nd^{3+} doped germanate glass for the possibility of its future photonic device applications. On the basis of Judd–Ofelt (*J–O*) theory [17,18], absorption spectrum has been analyzed and three *J–O* intensity parameters Ω_λ ($\lambda = 2, 4, 6$) were determined. Moreover, radiative properties have been discussed in detail, involving spontaneous transition probability (A_{rad}), radiative lifetime (τ_{rad}), fluorescence branching ratios (β_{rad}) and stimulated emission cross section (σ_{em}). In addition, thermal stability was also studied to estimate the potential application of the germanate glass.

2. Experimental details

The investigated germanate glass has the following molar compositions as $65GeO_2$–$8Ga_2O_3$–$17BaF_2$–$5La_2O_3$–$5Li_2O$–$1Nd_2O_3$ and the sample was prepared via using a conventional melt-quenching technique in air atmosphere. High-purity GeO_2 (99.999%), Ga_2O_3 (99.99%), BaF_2 (99.95%), La_2O_3 (99.99%), Li_2O (99%) and Nd_2O_3 (99.999%) powders were used to prepare germanate glass. Raw materials about 20 g were mixed homogeneously firstly and then put in an alumina crucible. Subsequently, the covered alumina crucible was heated in an electric furnace at 1350 °C for 50 min. Finally, the well-melted glassy liquid was poured onto a preheated steel plate (the steel plate has the temperature below the glass transition point.) and quickly moved to a furnace with the temperature around the glass transition temperature (T_g). The annealed sample was cut and polished into the size of 10 mm × 10 mm × 1.5 mm for the optical property measurements.

Refractive index of the glass host was measured by prism minimum deviation method and the value was 1.69. The density was tested by Archimedes method using distilled water as immersion liquid and the glass density was measured to be 4.35 g cm^{-3}. Differential scanning calorimeter (DSC) curve of the glass host were measured using NETZSCH DTA 404 PC at the heating rate of 10 K/min with maximum error of ±5 °C. The absorption spectrum was obtained using a JASCO V-570UV/VIS spectrophotometer at room temperature. The emission spectrum was recorded by pumping the sample with 808 nm laser diode (LD). The lifetime of 1.05 μm emission was determined by a combined fluorescence lifetime and steady state spectrometer (FLSP 920) (Edingburg Co., England) and detected with a liquid-nitrogen-cooled PbS detector.

3. Results and discussion

3.1. Thermal stability of glass host

Fig. 1 shows the DSC curve of germanate glass host. According to thermal analysis, it is found that the glass transition temperature (T_g) and onset crystallization temperature (T_x) can be as high as 554 °C and 667 °C, respectively. It has been reported that high T_g value can resist thermal damage effectively since the high power densities associated with pulsed lasers may lead to rapid local heating or melting of glass [19]. The T_g of present sample is much higher than those of tellurite (351–460 °C) [20], bismuth (401 °C) [21] and fluoride glass (332 °C) [22], while it is a little lower than that of other reported germanate glass (618 °C) [14]. In order to evaluate thermal stability of glass quantitatively, a parameter is usually employed as follows [23].

$$\Delta T = T_x - T_g \quad (1)$$

The higher the ΔT is, the better the glass thermal stability and ability to resist crystallization are. Additionally, the glass forming factor developed by Hruby is more suitable for estimating the glass thermal stability than ΔT, which is defined as [14].

$$k_{gl} = (T_x - T_g)/(T_m - T_g) \quad (2)$$

where T_m is the melting temperature of glass and here is 1350 °C. From Fig. 1, it is calculated that the parameters of thermal stability ΔT and k_{gl} are 113 °C and 0.142, respectively. They are larger than those of fluoride glass (76 °C and 0.133) [22] and are comparable with those of other reported germanate glass (129 °C and 0.176) [14]. The results reveal that the prepared germanate glass possesses good thermal stability to resist thermal damage at high pumping intensities and anti-crystallization property.

3.2. Absorption and radiative properties

Fig. 2 presents the room temperature absorption spectrum in the range of 300–1000 nm in Nd^{3+} doped germanate glass. Eleven absorption bands are observed, which are assigned to the transitions $^4I_{9/2} \rightarrow {}^4D_{7/2}$, $^4D_{3/2,5/2}$, $^2D_{3/2}$, ($^2P_{1/2}$, $^2D_{5/2}$), ($^4G_{11/2}$, $^2G_{9/2}$, $^2K_{15/2}$), $^4G_{9/2}$, ($^4G_{7/2}$, $^2K_{13/2}$), ($^4G_{5/2}$, $^2G_{7/2}$), $^2H_{11/2}$, $^4F_{9/2}$, ($^4F_{7/2}$, $^4S_{3/2}$), ($^4F_{5/2}$, $^2H_{9/2}$) and $^4S_{3/2}$ at 328, 357, 379, 429, 473, 512, 525, 583, 623, 681, 747, 804, 876 nm, respectively. The assignments of these transitions have been made on the basis of Carnell [24]. The absorption spectrum of present work is very similar to those of other reported Nd^{3+} doped glass systems except for some small changes in the peak position and relative intensities [1,2,25]. This can be ascribed to the nature of various ligand fields of different glass matrixes. It is noted that the absorption band around 808 nm due to the $^4I_{9/2} \rightarrow$ ($^4F_{5/2}$, $^2H_{9/2}$) transition is very obvious and has higher absorption coefficient compared with other transitions indicating that Nd^{3+} doped germanate glass can be excited by 808 nm LD.

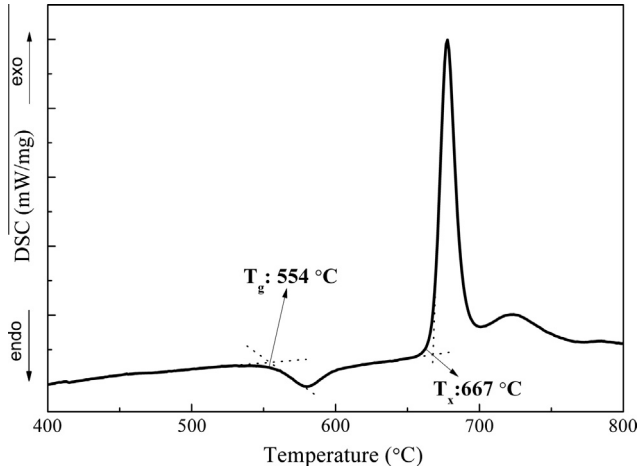

Fig. 1. The DSC curve of germanate glass host.

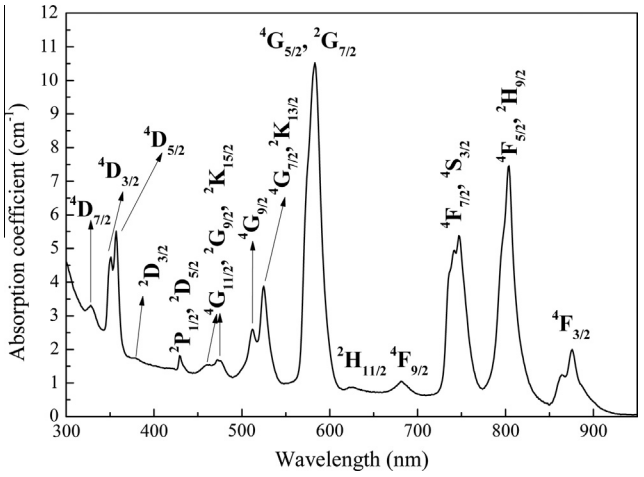

Fig. 2. Absorption spectrum in Nd^{3+} doped germanate glass.