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Compositional effects of Na_2O, GeO_2, and Bi_2O_3 on 1.8 μm spectroscopic properties of Tm^{3+} doped zinc tellurite glasses

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ABSTRACT

Compositional effects of Na_2O, GeO_2, and Bi_2O_3 on 1.8 μm spectroscopic properties have been investigated to enhance 1.8 μm emission in Tm^{3+} doped zinc tellurite glasses. It is found that the heightened impact of Bi_2O_3 on 1.8 μm emission is more prominent than that of Na_2O and GeO_2. Furthermore, the partial substitution of Bi_2O_3 makes the lifetime of Tm^{3+}:$^3F_4$ level increase from 547 μs to 671 μs while Na_2O and GeO_2 have almost no effect on the lifetime. Relative energy transfer mechanism is analyzed and absorption and emission cross sections of the Tm^{3+}:$^3F_4 \rightarrow {}^3H_6$ transition are determined. The changes in density, refractive index, and thermal properties are also observed with the partial substitution of these compositions for ZnO. Especially, the glass thermal stability is obviously improved after the partial substitution. These results indicate that Tm^{3+} doped zinc tellurite glasses containing Bi_2O_3 appear to be an excellent host material to achieve 2.0 μm laser.

1. Introduction

Since several chemical compounds (H_2O, CO_2, N_2O, etc.) are endowed with many absorption lines at eye-safe 2.0 μm spectral region [1], a solid state laser source operating at this region has recently attracted numerous interest and thus offers potential applications in eye-safe lidar, high-resolution molecular spectroscopy, biomedical systems, remote sensing, and pump sources as mid-infrared lasers and optical parametric oscillators [2–4]. In pursuit of this efficient, compact, and cheap laser, Tm^{3+} doped glasses have been considered as an attractive candidate of the host material due to strong absorption band around the emission wavelength of commercial high-power 808 nm laser diode, efficient cross relaxation among Tm^{3+} ions, and larger inhomogeneous broadening in glasses. In fact, a number of various glass hosts such as silicate, fluoride, germanate, and tellurite glasses have achieved 2.0 μm laser [5–7]. Among these glass hosts, tellurite glasses are characterized by several superiorities including wide transmission region (typically 300–5000 nm), comparatively low maximum phonon energy (800 cm^{-1}), good chemical durability, high rare-earth (RE) ion solubility, and easy fabrication with low melting temperature [6]. Besides, they also have high refractive index (~2) which results in the increment of the absorption and emission cross sections of active ions, good optical properties, and inborn ability to drastically broaden emission spectrum of active ions due to the multiplicity of structural units. It is well known that TeO_2-ZnO glass system possesses wide glass-forming range and good chemical stability and has been used as a basis for multi-component optical glass synthesis [8]. Moreover, upconversion spectra properties in RE^{3+} doped TeO_2-ZnO glasses have been investigated and demonstrated to be very good due to relatively low maximum phonon energy [9–11]. However, there are few reports about 1.8 μm spectroscopic properties in Tm^{3+} doped TeO_2-ZnO glasses. Meanwhile, it is very important to add several oxides into Tm^{3+} doped TeO_2-ZnO glasses in terms of the improvement of thermal stability and 1.8 μm emission intensity.

Herein, we report compositional effects of Na_2O, GeO_2, and Bi_2O_3 on 1.8 μm spectroscopic properties of Tm^{3+} doped zinc tellurite glasses. Density, refractive index, thermal properties, absorption spectra, and emission spectra were measured along with the lifetime of Tm^{3+}:$^3F_4$ level. In addition, energy transfer mechanism is analyzed and absorption and emission cross sections of the Tm^{3+}: $^3F_4 \rightarrow {}^3H_6$ transition are determined.

2. Experimental

Tellurite glasses with the molar compositions of $75TeO_2 - 24.5ZnO$-$0.5Tm_2O_3$ and $75TeO_2 - 20ZnO$-$4.5R_xO_y - 0.5Tm_2O_3$ ($R_xO_y = Na_2O$, GeO_2, and Bi_2O_3) which are hereafter denoted as TZ, TZN, TZG, and TZB, respectively, were prepared by the conventional melt-quenching method. In addition, tellurite glasses with the molar compositions of $75TeO_2 - 24.5ZnO$-$0.5Bi_2O_3$, $75TeO_2 - 20ZnO$-$4.5Bi_2O_3 - 0.5Tm_2O_3$ and $75TeO_2 - 15ZnO$-$9.5Bi_2O_3 - 0.5Tm_2O_3$ were also prepared in order to investigate the role of Bi_2O_3. Appropriate amounts of these chemicals

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(~20 g) were well mixed and then melted in a platinum crucible at about 850 °C for 30 min in oxygen atmosphere. Then the melts were poured onto a preheated stainless steel plate and further annealed at 450 °C for 5 h, after which they were cooled slowly inside the furnace to room temperature. The annealed samples for the optical property measurements were cut into rectangular 20 × 10 × 1.5 mm^3 shapes and then polished. Densities of glasses were determined by the Archimedes' principle using the distilled water as the medium. The refractive index of all the samples was measured by the prism coupling method (Metricon Model 2010) at 632.8 nm with an error of $\pm 5 \times 10^{-4}$. The transition temperature (T_g) and onset crystallization temperature (T_x) were determined by a Netzsch STA 449C Jupiter different scanning calorimeter (DSC) at a heating rate of 10 °C/min from 25 °C to 700 °C under N_2 atmosphere. Optical absorption spectra measurements were performed on a Perkin-Elmer Lambda 900/UV/VIS/NIR spectrophotometer. The fluorescence spectra were recorded with a computer-controlled Triax 320 type spectrofluorimeter (Jobin-Yvon Corp.) equipped with an InAs detector upon the excitation of an 808 nm LD. Lifetime measurements were carried out by exciting the samples with an 808 nm LD. An InAs detector was used to detect the lifetime of Tm^{3+}:$^3F_4$ level (1.8 µm). All measurements were carried out at room temperature.

3. Results

Fig. 1 presents the refractive index (n) and density (ρ) of all the glasses. It is found that the refractive index increases with the partial substitution of Bi_2O_3 for ZnO, whereas it decreases with the partial substitution of Na_2O and GeO_2, compared with TZ glass. This can be explained by considering the fact that Bi_2O_3 possesses a higher polarizability and mole refraction than ZnO, which is beneficial to the enhancement of spontaneous emission probability and emission cross section of active ions. In addition, the density increases when ZnO is partially replaced by GeO_2 and Bi_2O_3, resulted from larger molar mass. However, the partial substitution of Na_2O makes the density drop.

Thermal stability is one of the important properties for glasses, especially in fiber drawing. The glass thermal stability can be estimated according to the characteristic temperatures, such as T_g and T_x which are determined from the DSC curves. $\triangle T = T_x - T_g$ has been frequently used as an approximate estimation of the glass thermal stability, which represents the temperature interval during the nucleation appearance. The larger $\triangle T$ is, the better the glass thermal stability becomes. Generally, glasses with a large $\triangle T$ above 100 °C will successfully facilitate the fiber drawing. Fig. 2 shows DSC curves of all the samples along with the values of T_g and $\triangle T$. It is clear from Fig. 2 that T_g increases with the partial substitution of GeO_2 and Bi_2O_3 for ZnO, while the partial substitution of Na_2O causes the decrement of T_g because Na_2O acts as network modifier that breaks the glass network, which is reflected by the decrease of the density and refractive index as shown in Fig. 1. In addition, $\triangle T$ increases with the partial substitution of Na_2O, GeO_2, and Bi_2O_3 and TZB has the highest $\triangle T$, indicating that the glass thermal stability is improved after the partial substitution. As a result, TZB glass is desirable for low-loss fiber fabrication in view of the glass thermal stability.

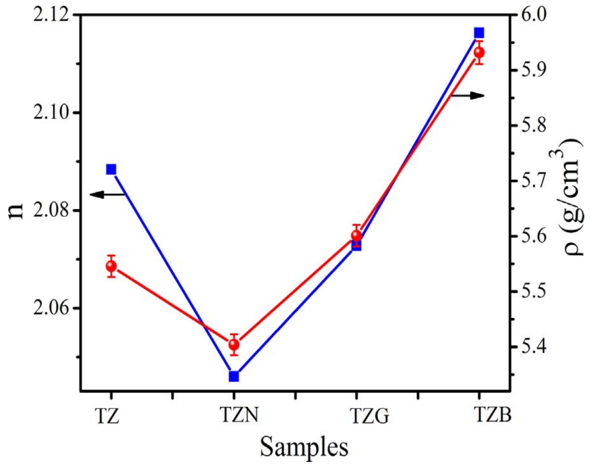

Fig. 1. Refractive index and density of all the glasses.

Fig. 3 presents the absorption spectra of TZ, TZN, TZG, and TZB glasses in the wavelength range from 400 to 2000 nm. The absorption spectrum is composed of five absorption bands of Tm^{3+} centered at 464, 686, 792, 1210, and 1698 nm, corresponding to respective transitions from the $^3H_6$ ground state to excited states $^1G_4$, $^3F_{2,3}$, $^3H_4$, $^3H_5$, and $^3F_4$. Energy levels above $^1G_4$ level are not clearly identified because of strong intrinsic bandgap absorption in the host glass. It is also noted that the position and shape of five absorption peaks remain unchanged when ZnO is partially replaced by Na_2O, GeO_2, and Bi_2O_3.

Fig. 4 compares the normalized fluorescence spectra in TZ, TZN, TZG, and TZB glasses pumped by 808 nm LD. It is noted that the spectra are characterized by two emission peaks located at 1450 and 1798 nm. Moreover, the emission intensity near 1.8 µm in TZB glass is the highest in all the glasses. The reason will be discussed in the next section.

4. Discussion

Two emission peaks at about 1450 and 1798 nm in Fig. 4 can be easily assigned to the Tm^{3+}:$^3H_4 \rightarrow {}^3F_4$ and $^3F_4 \rightarrow {}^3H_6$ transitions, respectively. It is observed that the emission intensity at 1798 nm is much stronger than the one at 1450 nm in all the samples, indicating efficient cross relaxation process (Tm^{3+}:$^3H_4 + {}^3H_6 \rightarrow 2{}^3F_4$) exists. It is worth noting that heightened impact of Bi_2O_3 and GeO_2 for 1.8 µm fluorescence is more prominent than that of Na_2O. The phenomenon may be related to the spontaneous emission rate of Tm^{3+}:$^3F_4 \rightarrow {}^3H_6$. According to J-O theory [12,13], the values of the spontaneous radiative transition probability in TZ, TZN, TZG and TZB are calculated and equal to 407.4, 432.8, 503.7 and 515.5 s^{-1}, respectively. High spontaneous radiative transition probability is favorable to intense 1.8 µm emission and offers a better possibility to achieve efficient laser actions [14]. Thus, the fluorescence enhancement occurs when ZnO is partially substituted by GeO_2 and Bi_2O_3.

The fluorescence decay curves of the $^3F_4 \rightarrow {}^3H_6$ transition in all the samples were measured, as shown in Fig. 5(a). It is clear that with the partial substitution of Bi_2O_3 for ZnO, the lifetime of Tm^{3+}:$^3F_4$ level obviously changes and increases from 547 µs to 671 µs while the variation in the lifetime is negligible with the partial substitution of Na_2O and GeO_2. It was reported that Bi_2O_3 acted as a sensitizer or activator in silicate glasses, germanate glasses, germanium silicate glasses and fluorogermanate glasses under 808 or 980 nm excitation [15–18]. This is due to the presence of broadband absorption from Bi which covers the near UV-to-NIR wavelength range and energy transfer from Bi to active ions. We carefully examined the optical absorption spectra in Bi_2O_3 singly doped tellurite glasses and found that a broadband absorption from Bi did not appear. This suggests that the role of Bi_2O_3 in tellurite glasses is different from that in other glasses. In addition, no fluorescence appeared in Bi_2O_3 singly doped tellurite glasses. It is very interesting that 1.8 µm fluorescence intensity from Tm^{3+} enhances when the content of Bi_2O_3 increases, which manifests that the addition of Bi_2O_3 is beneficial to 1.8 µm emission. We think that the reason for the lifetime extension with the addition of Bi_2O_3 may be the variation of the local environment of the Tm^{3+} ions in the matrix, which delays the population change in $^3F_4$ level. In addition, When Bi_2O_3 with lower phonon energy (~500 cm^{-1}) relative to that of tellurite glasses (~700 cm^{-1}) is added, the multiphonon decay rate decreases, which is favorable to the increase of the lifetime of Tm^{3+}:$^3F_4$ level. In order to give the core cause, we will proceed to do further research for Bi_2O_3 and Tm_2O_3 doped tellurite glasses.