



Effects of GeO₂ concentration on the absorption and fluorescence behaviors of Yb³⁺ in tellurite glasses



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ABSTRACT

Yb³⁺-doped tellurite glasses exhibited largest absorption and emission cross sections. However, it is more valuable to achieve larger Stark splitting of Yb³⁺ than improve the absorption and emission cross sections. In this work, we introduced a part of GeO₂ into tellurite glass matrix to enlarge the Stark splitting of Yb³⁺. The effects of GeO₂ concentration on the spectroscopic characteristic of Yb³⁺ were systematically investigated. The stimulated absorption and emission cross sections increased to be 1.62 pm² and 0.88 pm² when the GeO₂ concentration up to 30 mol%, then decreased with the GeO₂ concentration further increased. The Stark splitting of Yb³⁺ do not change until the GeO₂ concentration up to 30 mol%. The NIR fluorescence lifetimes of Yb³⁺ drastically decreased from 850 μs to 385 μs with the GeO₂ concentration increasing, which was due to the increasing multi-phonon relaxation rate and reabsorption. Intense NIR fluorescence were observed when excited by the ultraviolet light, which can be ascribed to the energy transfer from the CTB of Yb³⁺-O²⁻ couple to Yb³⁺. The CTB showed a slight blue-shift from 338 to 313 nm with GeO₂ concentration increasing, which was ascribed to the size of the cation site would increase.

1. Introduction

Among various oxide glasses, tellurite glasses exhibited some excellent optical properties, such as high refractive indexes, lowest phonon energy, wide transmittance from visible to mid-infrared, and easy fabrication. These advantages make it was suitable to be the host glass matrix for rare earth ions with good spectroscopic characteristics. In the past decades, rare earth ions doped tellurite glasses have showed wide applications in producing various light sources, such as Yb³⁺, Tm³⁺, Ho³⁺, Er³⁺-doped tellurite glass fiber has been widely applied in near and mid infrared fiber lasers [1–5]. Among these rare earth ions, Yb³⁺ has simple energy levels with a ground state ²F_{7/2} and an excited state ²F_{5/2} [6]. The ground state and excited state will Stark split into several sub-levels due to the effects of crystal-field. The simple energy level configuration of Yb³⁺ prevents the existence of several de-excitation processes, such as the excited state absorption, concentration quenching by down-conversion cross relaxation or upconversion, which make Yb³⁺-doped glasses advantages for high power lasers [7], such as Yb³⁺-doped phosphate [8], silicate [9], silica [10], germanate [11], fluorophosphate [12], and tellurite glasses [13]. Among these oxide glasses, Yb³⁺-doped tellurite glass has largest absorption and emission

cross sections, which was regarded as the optimal optical gain media to achieve high power laser in the past decades. However, Zhang et al. systematically studied the effects of Stark splitting of Yb³⁺ on the laser performance, and proposed that larger Stark splitting make the Yb³⁺-doped glass laser tends to operate close to quasi-four level scheme, while smaller Stark splitting of Yb³⁺ tends to operate close to quasi-three-level scheme [14,15]. In order to improve the laser efficiency, they proposed that it is more valuable to achieve larger Stark splitting of Yb³⁺ than improve the absorption and emission cross sections. The Stark splitting of Yb³⁺ was regarded to be largest in germanate glass, and smaller in tellurite glass. In this paper, we introduce a part of GeO₂ in the tellurite glass to improve the Stark splitting of Yb³⁺ and investigate the influence of GeO₂ on the fluorescence behaviors of Yb³⁺ in tellurite glasses.

More recently, Yb³⁺ ions activate downconversion luminescence materials have attracted extensive attentions, it was largely driven by its potential applications as spectrum convertors to improve the efficient of the solar cells through [16]. The near infrared quantum cutting via cooperative downconversion have been demonstrated in Ln³⁺-Yb³⁺ (Ln = Tb³⁺, Tm³⁺, Pr³⁺, Ho³⁺, Er³⁺, Dy³⁺, Nd³⁺) co-doped phosphors, glasses, and glass ceramics, where Ln³⁺ ions acting as

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absorption center, Yb^{3+} ions acting as acceptors [17–23]. While the absorption band of Ln^{3+} ions in the visible and ultraviolet region was rather narrow due to the nature of parity forbidden $4f-4f$ transitions [24]. Thus, loss of most part of practical solar spectrum. To maximum harvest the most of the solar spectrum, some activators with broadband absorption in the ultraviolet-visible region, such as Eu^{2+} , Ce^{3+} , Yb^{2+} , Bi^+ , Pb^{2+} or the host lattice, defect centers, charge-transfer, e.g. $\text{Ce}^{4+}-\text{Yb}^{2+}$ were employed to overcome the problem [25–30]. These works are focused on the maximum harvest the spectrum region of 400–500 nm, which is strongest in the AM 1.5 solar spectrum. The 300–400 nm shows low intensity than 400–500 nm in the AM 1.5 solar spectrum, but stronger in AM 0 solar spectrum. The broadband downconversion materials which maximum harvest the UV spectrum shows potential application in an extraterrestrial situation. Yb^{3+} single doped glasses exhibit a strong excitation band in the 300–400 nm region, then lead to efficient near infrared (NIR) emission, which has potential applications in solar cells operating in an extraterrestrial situation. Yb^{3+} -doped germanate, tellurite, silicon phosphors have demonstrated that the Yb^{3+} single doped materials have broadband absorption in the UV region and efficient emit photons with the wavelength at 920–1150 nm, where perfectly matching the strongest spectral of AM 0 solar spectrum and maximum spectral response of Si solar cells [31–33]. It is well known that Yb^{3+} has no absorption band in the UV region. The near infrared luminescence of Yb^{3+} when excited by UV light was definitely derived from the energy transfer from an UV absorption centers to the Yb^{3+} ions. Some researchers ascribed the UV absorption center to the $\text{Yb}^{3+}-\text{O}^{2-}$ charge transfer [31,33]. And the charge transfer band (CTB) depended on the host glass matrix. In this paper, we studied the effects of GeO_2 concentration on the position of the CTB in tellurite glasses, and we believe it would be benefit to the designation of Yb^{3+} singly doped high efficient down conversion materials.

2. Experimental

The sample glasses were prepared by the conventional melting method with the compositions (in mol%):

$$(75-x)\text{TeO}_2-20\text{ZnO}-5\text{Na}_2\text{O}-x\text{GeO}_2-2\text{Yb}_2\text{O}_3(x=0, 5, 15, 30, 60).$$

Analytical reagents Na_2CO_3 , ZnO and 4N TeO_2 , Yb_2O_3 , GeO_2 were used as starting materials. 30 g mixture of the raw materials was weighed according to the above nominal composition and homogeneously ground and mixed, and then was transferred into an alumina crucible. The melting temperature was 850 °C for the glasses with GeO_2 concentration were 0 and 5 mol%, 900 °C for the $x = 15$ mol%, 1100 °C for the $x = 30$ mol% and 1150 °C for the $x = 60$ mol%, respectively. All the samples were melted at corresponding temperature for 40 min, and casted on the stainless steel plate that was preheated at 300 °C, then were annealed at corresponding glass transition temperature for 3 h. The obtained glasses were cut into suitable size. Two big faces of each sample glass was polished for optical measurements.

Absorption spectra were measured with Lambda 900 spectrophotometer. Static emission spectra, fluorescence lifetime were measured with Edinburgh FLS920 Fluorospectrophotometer. All the measurements were performed at room temperature.

3. Results and discussions

Fig. 1 showed the absorption spectra of Yb^{3+} doped tellurite glasses with the GeO_2 concentration increases from 0 to 60 mol%. In the visible region, the transmission cutoff wavelength showed a slight blue-shift from about 400–350 nm with increasing GeO_2 concentration. The ultraviolet region absorption edge was derived from the transition from localized states at the top of the valence band to the delocalized states in the conduction band. Davis and Mott deduced a general form to describe the relationship between the photon energy and the

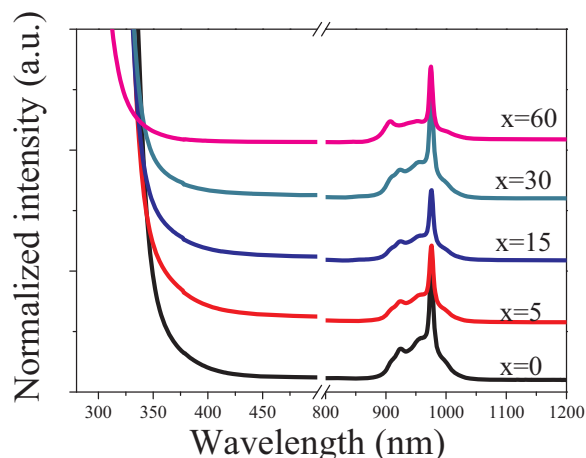


Fig. 1. Absorption spectra of Yb^{3+} doped tellurite glasses with the GeO_2 concentration from 0% to 60 mol%.

absorption [34]:

$$\alpha(\omega) = \frac{B}{\hbar\omega}(\hbar\omega - E_{opt})^r \quad (1)$$

where $\alpha(\omega)$ was the optical absorption coefficient, B was a constant, \hbar was the reduced Planck constant, $\omega = 2\pi\nu$ and E_{opt} was the optical energy gap, and r was an index which can assume values of 2, 3, 1/2, 3/2 depending on the nature of the electronic transitions responsible for the absorption. For tellurite glasses, the r was estimated to be 2 [34]. We re-plotted the optical absorption in terms of absorption by indirect transitions for tellurite glasses with increasing the GeO_2 concentration from 0 to 60 mol% in Fig. 2, and the E_{opt} can be obtained from the extrapolation of the linear portion of these curves. The value of the E_{opt} increased from 3.5 eV to 3.92 eV when the GeO_2 concentration increased from 0 to 60 mol%. The E_{opt} was represented as the transitions from localized states at the top of the valence band into the delocalized states in the conduction band or vice versa. Stevels had suggested that the movement of the ultraviolet absorption band to longer wavelengths corresponding to transitions from the non-bridging oxygen which bind an excited electron less tightly than a bridging oxygen [35]. When germanium atoms was introduced into glass structure, it would tend to form GeO_4 tetrahedra, while tellurium would forms not only TeO_4 tetrahedra, but also TeO_{4-x} units [36,37]. Thus, when the GeO_2 concentration increased from 0 to 60 mol%, the non-bridging oxygen ions content decreased, shifting the band edge to higher energies and leading to an increase in the value of E_{opt} .

The stimulated absorption cross sections around 976 nm were

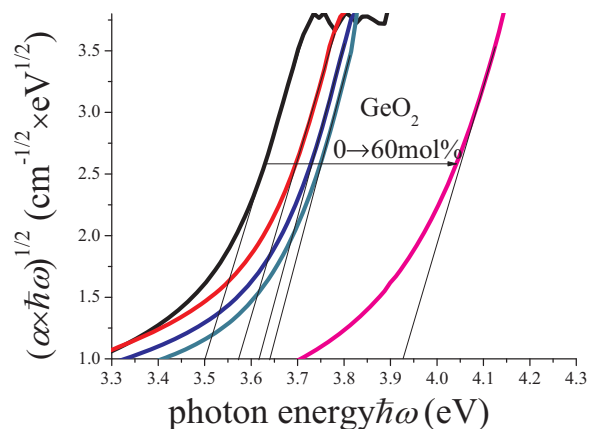


Fig. 2. Optical absorption re-plotted in terms of absorption by indirect transitions for tellurite glasses with the GeO_2 concentration from 0 to 60 mol%.

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