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Pr^{3+}/Er^{3+} co-doped tellurite glass with ultra-broadband near-infrared fluorescence emission

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ABSTRACT

Pr^{3+}/Er^{3+} co-doped tellurite glass with composition $80TeO_2$-$10Na_2O$-$5WO_3$-$5Nb_2O_5$ was synthesized by the conventional melt-quenching technique, and the obtained glass was characterized by the UV/Vis/NIR absorption spectrum, near-infrared fluorescence spectrum, differential scanning calorimeter (DSC) curve, X-Ray diffraction (XRD) pattern and Raman spectrum. Under the 488 nm excitation, it was found that Pr^{3+}/Er^{3+} co-doped tellurite glass could emit an ultra-broadband near-infrared fluorescence which extended from 1200 to 1650 nm with full-width at half-maximum (FWHM) of about 236 nm, and this ultra-broadband fluorescence was contributed by the multichannel emissions of Pr^{3+} and 1.53 μm band emission of Er^{3+}. The luminescent mechanism and energy transfer processes between Pr^{3+} and Er^{3+} ions which are responsible for the observed ultra-broadband fluorescence were analyzed. Meanwhile, optical absorption bands that are assigned with corresponding electronic transitions with respect to Pr^{3+} and Er^{3+} ions were identified from the measured absorption spectrum, and based on the optical absorption data, the gain coefficient and important spectroscopic parameters like Judd-Ofelt intensity parameter, spontaneous radiative transition probability, radiative lifetime and branching ratio were calculated to elucidate the radiative properties of doped rare-earth ions. In addition, the DSC curve exhibited the good thermal stability of glass host with $\Delta T > 150$ °C, Raman spectral study displayed the presence of different vibrational groups and XRD pattern confirmed the amorphous structural nature of the prepared glass. The present results indicate that Pr^{3+}/Er^{3+} co-doped tellurite glass is promising for the ultra-broadband near-infrared band fiber amplifiers covering the expanded low-loss communication window.

1. Introduction

With the progress of optical fiber communication technology, optical transmission system with channel rate of terabit per second is no longer far-fetched, however, many new occurred data services such as three-dimensional high-definition television, cloud computing and virtual-reality applications require extra optical channel bandwidth [1,2]. Fortunately, the modern fiber manufacturing technique brings availability of hydroxyl (OH^-) free transmission fiber based on silica glass with low-loss region from O-band to U-band. Therefore, developing the ultra-broadband near-infrared band luminescence sources for broadband fiber amplifiers covering the expanded low-loss communication window (~ 1200 to 1700 nm) in wavelength division multiplexing (WDM) networks attracts considerable attentions [3–5].

Recently, a lot of surveys were focused on the transition metal and heavy metal ions, such as Bi^+ [6], Ni^+ [7], Cr^+ [8], Pb^{2+} [9] and Co^{2+} [10], owing to their potential ultra-broadband near-infrared band emissions. Nevertheless, the bandwidth and peak wavelength of these ultra-broadband emissions rely sensitively on the host material compositions as well as the excitation wavelengths. Up to now, there are few reports about the ultra-broadband luminescence from rare-earth doped glass systems, although they have played the important roles in current communication system such as optical amplifiers and lasers [11]. However, the conventional Er^{3+}-doped fiber amplifier (EDFA) is hard to meet the large transmission capacity requirement because of its less than 70 nm gain bandwidth (1530–1600 nm) [12–14]. Therefore, rare-earth co-doped schemes have been investigated to enlarge the bandwidth, for instance, Tm^{3+} is an advisable way to extend the bandwidth of EDFAs [15,16]. Similarly, apart from the known 1.30 and 1.60 μm band emissions [17,18], the 1.47 μm band emission of Pr^{3+} should also be taken into account, since it can provide an excellent complement to Er^{3+} in the left shoulder of its 1.53 μm band fluorescence, which makes them possible to achieve ultra-broadband near-infrared band emission in the Pr^{3+}/Er^{3+} co-doped systems [3,5], however, the luminescent mechanism of this ultra-broadband emission need to be further explored.

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The choice of host material is also important as the luminescent properties of doped rare-earth ions are susceptible to the chemical environment of glass host. Compared with other glass hosts that the literatures put forward, tellurite glass is characterized by a number of excellent properties such as wide transmission window (0.35–6 μm), good glass stability and corrosion resistance, large rare-earth ion solubility (10–50 times larger than in silica), low host phonon energy (~ 750 cm^{-1}) and high refractive index (~ 1.8–2.3) [19–23]. Meanwhile, it is known that both WO_3 and Nb_2O_5 oxides are good glass formers, and adding these two components into tellurite glass can enhance the thermal stability and the resistance for crystallization [24,25]. Therefore, in this paper WO_3 and Nb_2O_5 oxides are simultaneously incorporated with TeO_2 oxide to synthesize new Pr^{3+}/Er^{3+} co-doped tellurite glass, and the ultra-broadband luminescence and its mechanism under the excitation at 488 nm were investigated.

2. Experimental procedures

The Pr^{3+}/Er^{3+} co-doped tellurite glass composed of $80TeO_2$-$10Na_2O$-$5WO_3$-$5Nb_2O_5$-xPr_2O_3-yEr_2O_3 ($x = 0.3$, $y = 0$; and $x = 0$, 0.3, $y = 0.1$ mol%) were prepared by conventional melt-quenching technique. The starting materials of TeO_2, Na_2O (introduced in Na_2CO_3 due to its stability), WO_3 and Nb_2O_5 were reagent grade, and Pr_2O_3 and Er_2O_3 were high purity with 99.99%. Hereafter, the prepared glass samples were respectively named as TWNP, TWNE, and TWNPE for a better readability. Batches of 10.0 g ingredient chemicals were weighed and ground thoroughly in an agate mortar to obtain homogeneous mixture. The well-mixed powder was placed in a platinum crucible and melted in an electric furnace at temperature of 900 °C for 1 h. The obtained melt was poured onto a brass mold preheated at 350 °C to avoid thermal shock and annealed for 2 h below the glass transition temperature to release mechanical stress and then cooled slowly down to the ambient temperature.

The prepared glasses were characterized by a series of physical and spectroscopic measurements which were carried out at room temperature, and the obtained some physical parameters are listed in Table 1. In which, the glass sample density was measured based on the Archimede's principle using pure water as an immersion liquid. The refractive index was measured using a prism coupler (Sairon Tech-SPA4000 TM) at a wavelength 632.8 nm. The thermal stability was evaluated using a differential scanning calorimeter (DSC) of TA Instrument Q2000 at a heating rate of 10 K/min. The powder X-ray diffraction (XRD) spectrum was recorded using a power diffractometer with Cu Ka radiation (40 kV × 25 mA) and a graphite monochromator. The Raman spectrum was measured with a Renishaw Micro-Raman instrument. The UV/Vis/NIR absorption spectrum was recorded by a Perkin-Elmer-Lambda 950 spectrophotometer. The near-infrared fluorescence emission spectrum was collected by Jobin Yvon Fluorolog spectrophotometer equipped with a photomultiplier tube (PMT) detector.

3. Results and discussion

3.1. Structural behavior and thermal stability

The obtained XRD spectra of Pr^{3+} single-doped (TWNP), Er^{3+} single-doped (TWNE) and Pr^{3+}/Er^{3+} co-doped (TWNPE) tellurite glasses are displayed in the inset of Fig. 1. It is shown that the XRD spectra possess nearly identical pattern with one broad hump at low angle but no any discrete or sharp diffraction peaks, which are typical for the amorphous state structural materials.

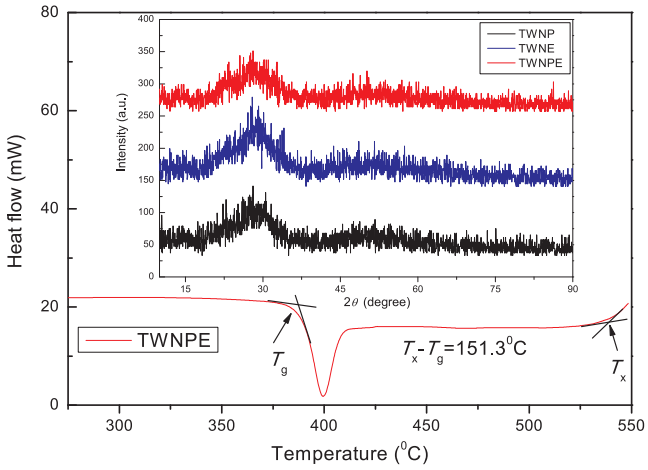

Fig. 1. The DSC curve of TWNPE glass and the inset is the XRD patterns of the powder TWN*x* (*x*→E, P, PE) glass samples.

Thermal stability is important for glass material when applied for fiber drawing or device preparation, which is characterized by technological parameter $\Delta T (= T_x - T_g)$, i.e. the difference between the glass crystallization onset temperature (T_x) and transition temperature (T_g) [26–28]. A large ΔT indicates a strong inhibition of nucleation and crystallization, and also a large working temperature range of fiber drawing can be allowed. Obviously, it is desirable for a glass host to possess ΔT as large as possible. As representative, the measured DSC curve of TWNPE glass is displayed in Fig. 1, and the obtained ΔT including the T_g and T_x of all prepared glass samples are listed in Table 1. It is found that the ΔT is about 150 °C in this work and is larger than that of other glass systems [29,30], which indicates that the studied tellurite glass has better thermal stability.

3.2. Raman spectroscopy

Fig. 2 displays the measured Raman spectroscopy of TWNPE glass in the range of 400–1000 cm^{-1}, which reveals the information about vibrational mode frequencies and various structural units of glass matrix [31]. TeO_2 oxide incorporated in glass was associated with [$TeO_{3+\delta}$] trigonal pyramid and [TeO_4] trigonal bi-pyramid structural units, and the added small amount of WO_3 oxide made the glass possess with [WO_4] tetrahedral and [WO_6] octahedral structural units [32,33], while the Nb_2O_5 oxide brought the [NbO_4] tetrahedral and [NbO_6] octahedral structural units, and the active NbO_6 octahedra can not only broaden the bandwidth but also enhance the nonlinearity because of its hyperpolarizability [34]. In short, the different spatial distributions of the three types of structural units will result in different ligand field strengths and effects on the doped rare-earth ions. The dotted lines in different colors in the Fig. 2 are the deconvolved Raman sub-peaks, in

Table 1
The refractive index (*n*), thickness (*d*, mm), density (ρ, g/cm^3), concentration (*N*, × 10^{20}/cm^3), glass transition temperature (T_g), crystallization onset temperature (T_x) and the difference ($\Delta T = T_x - T_g$) of the studied glass samples.

Glass	*n*	*d*	ρ	*N* (Pr^{3+})	*N* (Er^{3+})	T_g	T_x	ΔT	Ref.
TWNP	2.010	1.78	4.63	1.01	–	389.6	540.3	150.5	present
TWNE	2.012	1.80	4.69	–	0.35	387.7	538.1	150.4	present
TWNPE	2.015	1.80	4.73	1.03	0.34	388.5	539.8	151.3	present
Li_2O-Li_2WO_4-TiO_2-P_2O_5	–	–	–	–	–	425.0	532.0	108.0	[29]
B_2O_3-TeO_2-MoO_3- ZnO-Na_2O-SrO	–	–	–	–	–	458.0	561.0	103.0	[30]