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Erbium-doped fluorotellurite titanate glasses for near infrared broadband amplifiers

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ABSTRACT

A novel Er^{3+}-doped fluorotellurite titanate glasses with the basic molar composition $75TeO_2$- $5Nb_2O_5$- $5Bi_2O_3$- $5TiO_2$- $10PbF_2$, $75TeO_2$- $5Nb_2O_5$- $5Bi_2O_3$- $5TiO_2$- $10PbF_2$- 10000 ppm Er_2O_3 and $75TeO_2$- $5Nb_2O_5$- $5Bi_2O_3$- $5TiO_2$- $10PbF_2$- 20000 ppm Er_2O_3 are explored with respect to possible applications as optical amplifiers. Their thermal and optical features were determined using differential scanning calorimetric (DSC), and UV–Vis–NIR spectroscopy, respectively. The glasses transition temperature T_g, factor against crystallization S, optical energy gap and quantum efficiency were determined. Judd-Oflet parameters Ω_t (t = 2, 4, 6), branching ratio, β, fluorescence full width at half maximum (FWHM) of NIR emission, and life time τ, of $I_{13/2}$ level have been evaluated. The glasses were characterized by a higher values of FWHM of NIR emission at 1.53 μm under excitation by wavelength 980 nm with respect to other glasses system doped by single Er^{3+} ions. In the future these glasses can be fabricated as broadband fiber amplifier for the optical communication devices. The glasses studied glasses exhibit green emission under excitation wavelength of 445 nm.

1. Introduction

Optical amplifiers are used in a wide spectral range of optical communication window, especially for Wavelength Division Multiplexing (WDM) to create flexible transmission capacity and a huge number of channels in optical network system. Oxide glasses are very promising sources with broadband emission in the near infrared (NIR) spectral region for application as optical amplifiers operating in telecommunication window as well as for up-conversion lasers [1]. This window is shared into Short band (S- band), Centre band (C- band) and Long band (L-band). It is well known that erbium (Er^{3+}) ions are used in C + L-bands for optical amplification due to $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition at 1530 nm under excitation at wavelength 976 nm. Although Erbium doped fiber amplifier (EDFA) is a mature technology and is the workhorse for wavelength division multiplexing (WDM) and all optical networks, its relatively large size requires further research and development to achieve the desired small, compact, and efficient fiber amplifiers. It seems that TeO_2 based glasses are exceptionally promising host materials for optical amplifier due to their excellent properties such as relatively high refractive indices, good thermal stability, low phonon energy, low melting point, good corrosion resistance and transparency in a wide spectral region (from 0.3 up to 7 μm) [1–6]. Moreover tellurite glasses are also suitable candidates because they exhibit an inherently broad Er^{3+} gain band, offering 80 nm of usable bandwidth much broader than phosphate and fluoride glasses [7,8]. Er^{3+} doped tellurite glasses exhibits the highest emission cross section in the whole wavelength region. The stimulated emission cross section ($ó_{21}$) for Er^{3+} -doped telluride glass has been measured to be 6.44×10^{-25} m^2 [6], much larger than that in Er^{3+} -doped Al/P silicate materials (5.7×10^{-25} m^2) [8,9]. It is reported that the values of

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full width half maximum (FWHM) of emission at 1.5 μm are 44, 65 and 85 nm for Al/P silica [7], fluozirconate [8,9] and tellurite glass host [10] respectively. The Er^{3+} emission spectrum in TeO_2-ZnO-Na_2O (TZN) tellurite glasses is significantly spectrally broader (75 nm FWHM) with respect to other glasses studied as potential Erbium doped fiber amplifiers (EDFA) hosts [11]. G. Lakshminarayana et al. [12] have reported the NIR Luminescence from Er^{3+}/Yb^{3+} Er^{3+}/Tm^{3+} ions doped zincoborotellurite glass and have shown full width at half maxima (FWHM) around 58 nm and 87 nm for $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition, respectively. Also they reported that Er^{3+} doped glasses form the 70 TeO_2- 10 ZnO- 10 WO_3- 5 TiO_2- 5 Na_2O glass system has a broad emission band centered at 1535 nm ($^4I_{13/2} \rightarrow {}^4I_{15/2}$) with FWHM around wavelength 100 nm obtained under 980 nm LD excitation. Hence the design and search of the new compositions of host glasses matrix is very important for the enhancement of the amplification bandwidth. It is worth to notice that tellurite glasses doped with heavy metal oxide easily polarized (Bi^{3+}, Pb^{2+}) with empty d orbital (Ti^{4+}, Nb^{5+}) should lead to higher third order nonlinear optical susceptibility (NLO) properties compared with other TeO_2 glasses [13–19]. Therefore in this report we explore thermal and optical properties of Er^{3+} doped host glasses for composition TeO_2- Nb_2O_3- Bi_2O_3- TiO_2- PbF_2 to extend broadband emission FWHM for developing infrared lasers and optical amplifier.

2. Experimental

The glasses consists of composition with following content (in mol %): 75 TeO_2- 5 Nb_2O_5- 5Bi_2O_3- 5TiO_2- 10PbF_2, (S1), 75TeO_2- 5Nb_2O_5- 5Bi_2O_3- 5TiO_2- 10PbF_2- 10000 ppm Er_2O_3 (S2) and 75TeO_2- 5 Nb_2O_5- 5 Bi_2O_3- 5 TiO_2- 10 PbF_2- 20000 ppm Er_2O_3 (S3). The densities of the studied glasses were determined using the Archimedes method. For spectroscopic measurements, the glass samples were sliced and polished to parallelepipeds with dimensions of about 10 × 10 × 2 mm^3. The thermal characteristics of the glasses obtained were determined with use of differential scanning calorimetry (DSC) (NETZSCH 5). The transmission, absorption and reflection spectra of glasses tested were recorded with a Perkin-Elmer Lambda 900 spectrophotometer with spectral resolution of about 1 nm. The photoluminescence spectra were measured applying an Optron Dong Woo fluorometer system; the luminescence decay curves were measured following a short pulse excitation provided by an optical parametric oscillator pumped by a third harmonic of a nanosecond Nd:YAG laser. The chemical formula of glasses tested is shown in Table 1.

3. Results and discussion

In this work we prepared glasses of composition in mol% 75TeO_2- 5Nb_2O_5- 5Bi_2O_3- 5TiO_2- 10PbF_2(S1), 75TeO_2- 5Nb_2O_5- 5Bi_2O_3- 5TiO_2- 10PbF_2 – 10000 ppm Er_2O_3 (S2) and 75TeO_2- 5Nb_2O_5- 5Bi_2O_3- 5TiO_2- 10PbF_2- 20000 ppm (S3) with high optical homogeneity and high transparency (see Fig. 1).

The glass transition temperature (T_g), onset crystallization temperature T_c, first peak of crystallization T_{p1}, second peak of crystallization T_{p2}, melting point T_m, and thermal stability parameter $\Delta T = (T_c - T_g)$ were determined from DSC curves (see Fig. 2). Moreover thermal stability factor against crystallization S, were determined from

Table 1
The composition in mol%, and density of glasses studied.

Sample code	Glass matrix composition (mol%)	ρ in (g·cm^{-3})
S1	75TeO_2- 5Nb_2O_5- 5Bi_2O_3- 5TiO_2- 10PbF_2	5.8547
S2	75TeO_2- 5Nb_2O_5- 5Bi_2O_3- 5TiO_2- 10PbF_2- 10000 ppm Er_2O_3	5.7723
S3	75TeO_2- 5Nb_2O_5- 5Bi_2O_3- 5TiO_2- 10PbF_2- 20000 ppm Er_2O_3	5.7171

Table 2
Glass transition temperature (T_g), onset o crystallization (T_c) first peak of crystallization (T_{p1}) second peak of crystallization (Tp_2), melting point (T_m), and factor against crystallization (S) of glasses studied.

Sample Code	T_g [^{0}C]	T_x [^{0}C]	ΔT [^{0}C]	Tp_1 [^{0}C]	Tp_2 [^{0}C]	T_m [^{0}C]	S [^{0}C]
S1	330	385	55	410	472	667	4.16
S2	337	388	51	414	478	664	3.94
S3	340	393	53	417	488	660	3.74

the following equation; $S = \frac{\Delta T \cdot \left(T_{p1} - T_C\right)}{T_g}$. The thermal characteristics such as T_g, T_c, T_{p1}, T_{p2}, T_m, ΔT and S are summarized in Table (2). The values of ΔT, and S parameters are varied within the range 55 - 51 °C and from 4.16 to 3.74, respectively. The values of thermal stability parameter and factor against crystallization of the glasses studied are similar to those calculated for fluoride glass variation, ZBLAN glasses and chalcogenide glasses otherwise slightly lower in comparison with other tellurite glasses [19–22]. The glasses have relatively low value of factor against crystallization, which is a principal advantage to obtain transparent glass ceramics through the heat treatment of glass matrix performed near the glass transition temperature. From the presented results it can be seen that the value of the glass transition temperature T_g, increases from 330 to 340 °C when Er^{3+} ions content increased from 0 to 20000 ppm. The increased in the T_g values that was induced by the addition of Er_2O_3 could be explained be the increased degree of polymerization. Glass transition temperature values give also information on the rigidity of the tellurite glass network. The observed increase of Tg implies an increase in the rigidity of the tellurite glass network. The glasses studied have large value of T_g, what is a major advantage to resist thermal damage in photonic devices application caused by pumping of laser source. Moreover a high value of Tg temperature is crucial also for the different laser operated optical devices and triggers.

Fig. 3 shows the transmittance and reflectance spectra of prepared glasses with the compositions of 75TeO_2- 5 Nb_2O_5- 5 Bi_2O_3- 5 TiO_2- 10 PbF_2 (S1), 75 TeO_2- 5 Nb_2O_5- 5 Bi_2O_3- 5 TiO_2- 10 PbF_2 – 10000 ppm Er_2O_3 (S2) and 75TeO_2- 5Nb_2O_5- 5Bi_2O_3- 5TiO_2- 10PbF_2- 20000 ppm (S3) in mol%. It is established that the intensity of transmission of glasses is in the range 76–77%, decreases with increasing Er^{3+} ions from 0 to 20000 ppm. The variation of spectral dependence optical absorption coefficient α in spectral range 300–2500 nm and versus energy $h\nu$ in eV for the glasses studied is shown in Fig. 4a, b. The absorption coefficient α was determined from the following expression; $\alpha(\nu) = \frac{2.303.A}{l}$, where, A is the absorbance and, l, is the thickness. From Fig. 3 and Figure 4a, b one can see that upon doping the absorption edge of glasses is spectrally shifted towards higher wavelength. From the previous studies of fluorotellurite glasses [20–22], it can be denoted that when PbF_2 is introduced into the oxide glass matrices TeO_2- Nb_2O_5- Bi_2O_3- TiO_2, F^- ions are replaced by O^{2-} ions in (TeO)n units forming Te(O,F)n such as $Te(O,F)_{3+1}$ and $Te(O, F)_3$. This one confirms that the structural units of glasses were transformed from TeO_4 to $Te(O, F)_4$ and then to $Te(O,F)_3$. Incorporation of Er^{3+} in the glass host creates more non-bridging oxygen's (NBOs) in structural unit Te(O, F)n. Hence it leads to an increase in the degree of localization of electrons due to increasing the donor center content in the glasses matrix. The increase in donor center with increasing Er^{3+} from 0 to 2000 ppm shifts the absorption edge towards higher wavelength as is shown in Fig. 4a. The absorption spectrum consists of spectral bands with maxima at 1530, 976, 799, 652, 543, 521 and 488 nm corresponding to absorption transition from the ground state $^4I_{15/2}$ to $^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$ and $^4F_{7/2}$ respectively (see Fig. 4). Similarly these transition levels are attributed to the energy in cm^{-1} as follow; 6540, 10245, 12515, 15337, 18416, 19193 and 20491 cm^{-1}.

From the analysis of the absorption spectra near to the absorption