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Spectroscopic properties in Er^{3+} doped zinc- and tungsten-modified tellurite glasses for 2.7 μm laser materials

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ABSTRACT

This work reports the effect of different modifiers (ZnO/WO_3) on the thermal properties and mid-infrared emission of 2.7 μm in Er^{3+}-doped tellurite glasses. The Judd–Ofelt parameters, radiative transition probability, radiative lifetime and branching ratio of prepared samples are calculated and discussed. It is found that the present tungsten-modified tellurite glass doped with Er^{3+} possesses large calculated emission cross section around 2.7 μm (2.03×10^{-20} cm^2). The advantageous spectroscopic characteristics as well as good thermal stability suggest that the present glasses have potential applications for 2.7 μm laser materials.

1. Introduction

Mid-infrared (mid-IR) wavelengths lasers, especially fiber lasers at around 3 μm, are being driven by numerous applications in a wide range of fields including remote sensing, environmental monitoring, bio-engineering, medical diagnostics, etc [1,2]. The 2.7 μm emission of Er^{3+} ion corresponding to the $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition is closely linked to the above applications. However, Er^{3+} suffers from self-terminating of the $^4I_{11/2}$ level because of the much shorter lifetime of the emitting level ($^4I_{11/2}$) as compared to the terminal laser level ($^4I_{13/2}$). This can be overcome by increasing the doping density of erbium to use cross relaxation to empty $^4I_{13/2}$ state. Therefore it has been intensely investigated recently [3–5].

Glass continues to attract a high level of research and develop interests for rare-earth (RE) doped hosts due to its ease of fabrication and ability to be used as diode-pumped high-power solid state laser hosts, sensors, and optical amplifiers, etc. Previous efforts [6,7] have mainly been paid to the fluoride and chalcohalide glasses. Works concerned with 2.7 μm of Er^{3+} doped tellurite glasses are scarce [8]. Compared to other glasses, tellurite glasses are characterized with good chemical durability, high refractive index, high transmittance in near to middle infrared regions, and also high solubility for rare earth ions [9–12]. The high refractive indices greater than 2.0 result in large stimulated emission cross sections and the typically low phonon energies of 700–800 cm^{-1} result in low non-radiative decay rates. A considerable number of publications [9,13–16] dealing with the properties of tellurite glasses have been published for many TeO_2-based systems glasses. As is reported [17,18], TeO_2–ZnO and TeO_2–WO_3 glasses have relative wider glass-forming regions, and it is feasible to achieve good qualities by adjusting the components in these two systems. It is also known that both WO_3 and ZnO are good glass modifiers and adding these two components into tellurite glass can enhance its thermal stability and then improve the resistance for crystallization.

In this work, the thermal stability, structural and spectral properties of Er^{3+} doped ZnO/WO_3-modified tellurite glasses have been investigated. Judd–Ofelt strength parameters Ω_λ (λ=2, 4, 6), the transition probabilities, exited state lifetimes and emission cross-sections are calculated from absorption and emission measurements by using the Judd–Ofelt analysis and Fuchtbauer–Ladenburg equation. This work is aimed at the elucidation of the glass compositional influence on the spectroscopic properties in different tellurite glass systems and the discussion of the feasibility of zinc/tungsten-tellurite glasses as the candidates for a new type of Er^{3+}-doped 2.7 μm emission host materials.

2. Experimental

A series of zinc- and tungsten-modified tellurite glasses with a molar composition $90(TeO_2 + xZnO/WO_3)$-$10La_2O_3$, where x (15,20,

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and 25%) is the mol percent of ZnO/WO_3 and it ranges from 15 to 25, hereafter named TZy and TWy ($y=1$, 2 and 3), which were doped with 1 mol% Er_2O_3. All starting materials were reagent grade commercial powders with purity higher than 99.99%. The glasses were prepared by the melt quenching method. Well-mixed 15 g batches were melted in alumina crucibles at 900–1000 °C for 30 min while being bubbled with dry oxygen gas, and then the liquids were quenched in stainless-steel molds preheated near their glass transition temperatures and annealed for 2 h near the transition temperature and naturally cooled to room temperature. Samples for optical and spectroscopic properties measurements were polished with a thickness of 1 mm.

The refractive indexes of the samples were measured by the prism minimum deviation method. Three refraction indexes of three wavelengths (632.8 nm, 1064 nm, 1552 nm, respectively) for each sample were measured, and then we use the Cauchy dispersion formula to estimate the refractive index of other wavelengths: $n(\lambda)=a+b/\lambda^2+c/\lambda^4$,where a, b, c are constants in terms of the glasses, which can be calculated by the obtained three refractive index. The densities were measured by Archimedes method using distilled water as an immersion liquid. The characteristic temperatures were determined using NETZSCH STA 409PC differential scanning calorimeter (DSC). The absorption spectra were recorded by a Perkin-Elmer Lambda 900 UV/VIS/NIR spectrophotometer. The emission spectra were measured with an Edinburg FLSP920 type spectrometer. InGaAs detector for the emission spectrum measurement is used in this measurement and the pumping power is 0.84 W for all the samples. The Raman spectra were detected with a Renishaw invia Raman microscope in 100–1000 cm^{-1} using the 785 nm excitation line. All measurements were conducted at room temperature.

3. Results and discussion

The content of Al in our samples have been determined by means of ICP-AES (ICAP 6300) analysis. The results show the TZ samples contain up to 0.13 wt% Al and 0.98 wt% for TW samples due to the higher melting temperature. So the effect of alumina crucibles on the prepared samples can be negligible.

3.1. Raman analysis

In order to investigate the evolution of the glass structure with the component variation, Raman measurements are carried out on studied glass samples. Fig. 1 is the normalized Raman spectra of all the studied samples, which have been measured under 785 nm excitation lines. As we can see, the low frequency vibration bands ($<300\ cm^{-1}$) corresponding to the the vibration of the heavy metal cations (Te^{4+} in this case) and local structural groups(Te–O groups in this case) show no obvious change in the prepared samples [19]. Raman scattering band centered at around 450 cm^{-1} is assigned to the stretching vibrations of Te–O–Te linkages [20], which are formed by vertex sharing of TeO_4, TeO_{3+1} and TeO_3 polyhedra of the network backbone. The band of 678 cm^{-1} is assigned to the stretching vibrations of the TeO_4 trigonal bipyramidal (tbp) groups. They are linked through Te–O–Te, with O in a position alternatively axial and equatorial. While the bands at 770 cm^{-1} arises from TeO_3 and TeO_{3+1} vibration [21,22]. A strong band resolved around 930 cm^{-1} in TW samples is due to the vibrations of WO_3 (ν[WO_6] and ν_{as}[WO_6])[23]. A similar band found in the TZ samples which is much weaker can be assigned to the vibration modes of La^{3+}, Zn^{2+}[19]. The glasses contain a variety of structural motives (TeO_4, TeO_3, and TeO_{3+1}) due to the presence of Zn^{2+} modifier ions, which give rise to a large distribution of structural sites. As is shown in Fig. 1, the increasing concentration of Zn^{2+} modifiers in the glass would result in the formation of TeO_3 trigonal pyramids (tp) associated with non-bridging oxygen atoms (NBO) through an intermediate stage formation of TeO_{3+1} polyhedra. The intensity ratio of the stretching band of TeO_3 tp at 770 cm^{-1} and that of TeO_4 tbp at 678 cm^{-1} increased from 1.74 to 2.13 with increasing ZnO from 15 to 25 mol %. At the same time this ratio shows no obvious change with increasing WO_3.

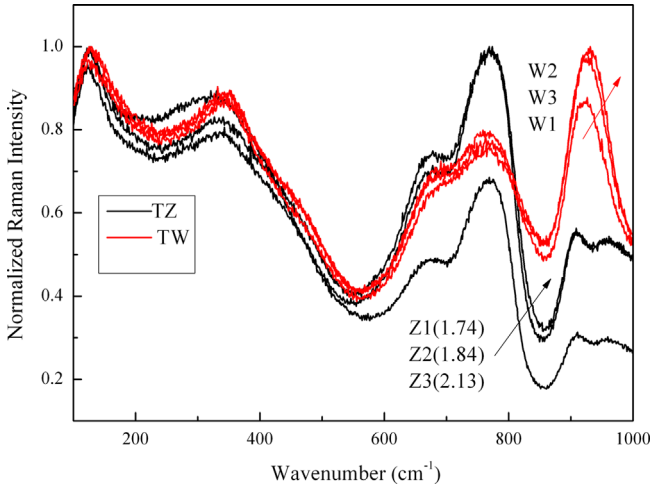

Fig. 1. Normalized room temperature Raman spectra of the glass samples.

3.2. Thermal properties

The thermal stability of glass samples is usually represented by three characteristic parameters: glass transition temperature (Tg), crystallization onset temperature (Tc) and the difference ΔT (Tc − Tg) between them. The values of Tc, Tg and the difference between Tg and Tc (ΔT=Tc − Tg) of the glasses are given in Table 1. As is shown in Table 1, the glass transition temperature does not show obvious changes with the addition of ZnO in zinc-modified tellurite glass nevertheless Tg values increase rapidly with WO_3 content in tungsten-modified tellurite glass. It is known that larger ΔT means strong inhibition to process of nucleation and crystallization. As is shown in Table 1, it is benefit for glass stability to increase ZnO content in zinc-modified tellurite glasses since ΔT of TZ1-TZ3 glasses increase from 152.3 °C to 222.2 °C with increasing ZnO from 15 mol% to 25 mol% and there is no obvious crystallization peak detected under a heating rate of 10 K/min^{-1} in the tungsten-modified tellurite glass samples indicating that these glasses are much preferable for performing fabrication and crystal-free fiber drawing.

The dependencies of physico-chemical properties on glass composition are shown in Table 1. As is seen from the table, for tellurite glasses, the values of the refractive index in 1064 nm, the density are increasing with the addition of glass modifiers

Table 1
Densities, refractive indexes and thermal properties of glass samples.

Samples	Density (g/cm^3)	Refractive indexes (632/1064/1552)	Tg (°C)	Tc (°C)	ΔT=Tc − Tg (°C)
TZ1	5.45	2.018/1.983/1.947	412.6	564.9	152.3
TZ2	5.55	2.007/1.979/1.943	411.7	604.9	193.2
TZ3	5.61	1.995/1.961/1.932	417.7	639.9	222.2
TW1	5.69	2.008/1.977/1.942	455.3	–	–
TW2	5.80	2.023/1.986/1.951	465.2	–	–
TW3	5.85	2.024/1.987/1.953	473.3	–	–