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Thermal analyses, spectral characterization and structural interpretation of Yb^{3+} doped TeO_2–ZnO–$ZnCl_2$ glasses

Guonian Wang [a,b,*], Junjie Zhang [a], Shixun Dai [a], Jianhu Yang [a], Zhonghong Jiang [a]

[a] *Department of Laserglass, Shanghai Institute of Optics & Fine Mechanics, Chinese Academy of Science, P.O. Box 800-211, Shanghai 201800, China*

[b] *Graduate School of the Chinese Academy of Science, P.O. Box 800-211, Shanghai 201800, China*

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Abstract

Bulk glasses have been prepared in the TeO_2–ZnO–$ZnCl_2$ systems. Their characteristic temperatures were determined and analyzed. Raman and FT–IR spectra were used to analyze the effect of $ZnCl_2$ on the structure and spectral properties of tellurite glasses and OH^- groups in this glass system. The spectroscopic properties including absorption spectra, emission cross-sections and fluorescence lifetimes of Yb^{3+} in TeO_2–ZnO–$ZnCl_2$ were measured and calculated. It is demonstrated that the progressive replacement less than 20 mol% of TeO_2 by $ZnCl_2$ improves the thermal stability, removes the OH^- groups, turns TeO_4 bi-pyramidal arrangement into TeO_3 (and/or TeO_{3+1}) trigonal pyramids structures and results in the decrease of the symmetry of the structure, which increases the emission cross-sections and lifetimes. But when the content of $ZnCl_2$ up to 30 mol%, the glass system becomes more hygroscopic and introduces more OH^- groups, which decrease the emission cross-sections and shorten the lifetimes. The results show that the glass system with $69TeO_2$–10ZnO–$20ZnCl_2$–$1Yb_2O_3$ is a desirable component for active laser media for high power generation.

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1. Introduction

The Yb^{3+} ion is of interest in lasers for the next generation nuclear fusion and as a sensitizer of energy transfer for infrared to visible upconversion and infrared lasers [1]. Yb^{3+}-doped glasses are materials capable of high peak power generation due to their high saturation fluencies, broad emission bandwidth and long upper-state lifetime. Levels of excited state configurations and charge transfer states of Yb^{3+} are in the ultraviolet. Therefore concentration quench-

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[*] Corresponding author.
E-mail address: wangwgn2942@mail.siom.ac.cn (G. Wang).

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ing and multiphoton relaxation should not affect the lasing or the excitation wavelength for Yb^{3+}-doped lasers [2]. This is an attractive feature for an optically pumped high-power laser. Since there is only the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition for Yb^{3+}, it is impossible to calculate directly the Judd–Ofelt parameters [3,4] like other rare-earth ions as Er^{3+}, Pr^{3+}, Nd^{3+} and Tm^{3+}. For this reason, the compositional dependence of the spectroscopic properties of Yb^{3+}-doped glasses is not well established. Up to now, there are only a few papers involving the effect of composition on the emission cross-section of Yb^{3+} in simple systems as borate, phosphate, silicate and fluoride phosphate glasses [5–7].

Tellurite glasses have been extensively investigated, mainly due to their interesting physical properties, but also from a fundamental point of view. Their unusually large infrared transparency, high linear and non-linear refractive indices, good thermal stability and corrosion resistance and suitability as a matrix for active element doping, represent the main justification for their continuous technological interest [8]. Recently, the literatures reported that Yb-doped tellurite glasses have more advantages over some other excellent laser glasses [9–11]: large absorption and emission cross-section, high Yb-doped concentration, wide fluorescence effective linewidth. However, the defects are evident such as low fluorescence lifetime and undesirable thermal stability. It is a key to improve the above-mentioned defects of tellurite glasses for their practical application.

TeO_2–ZnO binary system presents a broad glass-forming region, but glass formation in this system strongly depends on the cooling rate and the size of the melt, especially in the TeO_2-rich region [12]. The TeO_2–$ZnCl_2$ binary system was found to exhibit a continuous glass-forming region, yielding optically attractive stable and easy to prepare glasses [13]. However, zinc chloride is hygroscopic, unstable and difficult to handle. Based on the glass-forming ability of both TeO_2–ZnO and TeO_2–$ZnCl_2$ systems, in this Letter, we report on the experimental investigation of glass-forming ability, structure and spectral properties of Yb^{3+} doped TeO_2–ZnO–$ZnCl_2$ glass systems. The results demonstrate that the system of $69TeO_2$–10ZnO–$20ZnCl_2$–$1Yb_2O_3$ has desirable glass-forming ability, long fluorescence lifetime and high emission cross section, which can be acted as suitable materials for active laser media for high power generation.

2. Experimental procedures

Starting materials purer than 99.99% were mixed with component of $(89 - x)TeO_2$–10ZnO–$xZnCl_2$–$1.0Yb_2O_3$ ($x = 0$, 10, 20 and 30 mol%, named as TZC 0–3, respectively). Mixed batches were melted in platinum crucibles at 750–850 °C for ~ 30 min while being bubbled with dry air; then the liquids were poured into stainless-steel molds preheated near their glass transition temperatures and annealed for 2 h above glass transition temperature and then were annealed to room temperature in 48 h. Samples for optical and spectroscopic properties measurements were cut and polished to the size of $20 \times 10 \times 1\ mm^3$.

The index of refraction was measured at 486.1, 589.3 and 656.3 nm, with a precision V-prism refractometer using H_2 and Na lamps as spectral source. Cauchy's equation, $n(\lambda) = A + B/\lambda^2$, [14] was used to determine the refractive index at the mean wavelength of Yb^{3+}: $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition. Characteristic temperature T_g (glass transition temperature) and T_x (onset of the crystallization peaks) were determined from differential scanning calorimetry (DSC) measurements, carried out with powered samples in a Thermal Analyst 3100 calorimeter from TA Instruments, under N2 atmosphere at a constant heating rate being $10\ K\,min^{-1}$. The Raman spectra were recorded on a FT Raman spectrophotometer (Nicolet MODULE) within the range of 0–1200 cm^{-1}. Nd:YAG operating at 1064 nm is used as the excitation source, and the laser power level was 500 mW. The absorption spectra were measured using a Perkin–Elmer 900 spectrophotometer in the range 870–1100 nm at room temperature. Infrared (IR) transmission measurements were made using a Perkin–Elmer 1600 series FT–IR spectrometer from 6500 to 2500 cm^{-1} at intervals of 4 cm^{-1}. The emission spectra were obtained by exciting the samples with LD940 nm as pumping laser (excited at 940 nm). The relative errors in these emission measurements are estimated to be $< 5\%$. The fluorescence lifetimes were measured by exciting the samples with the same LD940 nm as above and detected by an S-1 photomultiplier tube.