ELSEVIER

Journal of Quantitative Spectroscopy & Radiative Transfer 98 (2006) 167–179

Journal of Quantitative Spectroscopy & Radiative Transfer

www.elsevier.com/locate/jqsrt

Energy transfer and infrared-to-visible upconversion luminescence of Er^{3+}/Yb^{3+}-codoped halide modified tellurite glasses

Q.Y. Zhang[a,*], Z.M. Feng[a], Z.M. Yang[a], Z.H. Jiang[a,b]

[a]*Key Laboratory of Specially Functional Materials of Ministry of Education and Institute of Optical Communication Materials, South China University of Technology, Guangzhou 510640, PR China*
[b]*Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 210800, PR China*

Received 11 August 2004; accepted 10 May 2005

Abstract

We report on the energy transfer and frequency upconversion spectroscopic properties of Er^{3+}-doped and Er^{3+}/Yb^{3+}-codoped TeO_2–ZnO–Na_2O–$PbCl_2$ halide modified tellurite glasses upon excitation with 808 and 978 nm laser diode. Three intense emissions centered at around 529, 546 and 657 nm, alongwith a very weak blue emission at 410 nm have clearly been observed for the Er^{3+}/Yb^{3+}-codoped halide modified tellurite glasses upon excitation at 978 nm and the involved mechanisms are explained. The quadratic dependence of fluorescence on excitation laser power confirms the fact that the two-photon contribute to the infrared to green–red upconversion emissions. And the blue upconversion at 410 nm involved a sequential three-photon absorption process.

Keywords: Glasses; Optical materials and properties; Halide modified tellurite glasses; Er^{3+}; Upconversion

*Corresponding author. Tel.: +86 20 87114204; fax: +86 20 87113823.
E-mail address: qyzhang@scut.edu.cn (Q.Y. Zhang).

0022-4073/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jqsrt.2005.05.081

1. Introduction

Tellurite glasses have extensively been investigated in the past several years due to its advantages such as a good transparency in the mid-infrared (0.35–6 μm), lowest phonon energy (700–800 cm^{-1}) among oxide glasses, high refractive index and high dielectric constants, good glass stability and rare-earth ions solubility [1–5]. In addition, tellurite glasses could be used in the production of optical fibers and planar waveguides. The combinations of tellurite and halide systems have further extended the families of optical glasses. Halide modified tellurite glasses provide more favorable situations with low phonon energy (halide glasses, phonon energy $<500\,cm^{-1}$) [6,7] and a relatively high thermal stability, high chemical durability and ease of fabrication (tellurite glasses). These special optical properties could be encouraged in identifying them as important materials for potential applications in high performance optics & laser technology and optical communication networks. On the other hand, there has been a continued effort toward the development of rare-earth-doped upconversion lasers in recent years, due to the possibility of infrared laser diode (LD) pumped UV-visible solid-state lasers, and the potential applications in the fields of optoelectronics, data storage and medical diagnostics, among many. In general, upconversion phenomenon is difficult to generate in conventional oxide glasses due to their high phonon energies ($>1000\,cm^{-1}$), corresponding to the stretching vibrations of the oxide glass network former. However, oxide glasses possess attractive properties like high chemical durability and ease of fabrication. Upconversion fluorescence has recently been reported in Er^{3+}-doped tellurite glasses [5,8–11]. However, only a few reports are available on the study of upconversion luminescence of Er^{3+}-doped halide modified tellurite glasses to the best of our knowledge. The main objective of this work is to carry on the development and a detailed study on the energy transfer (ET) and frequency upconversion properties of Er^{3+}-doped and Er^{3+}/Yb^{3+}-codoped TeO_2–ZnO–Na_2O–$PbCl_2$ halide modified tellurite glasses upon excitation with 808 and 978 nm LD, to elucidate its mechanisms responsible in the upconversion emission process, and to examine its suitability as potential optical glasses. Addition of Na_2O into glasses also provides suitability for the fabrication of optical waveguide devices by ion exchange.

2. Experiments

Halide modified tellurite glasses with the molar composition of $60TeO_2$–$20ZnO$–$5Na_2O$–$15PbCl_2$–$0.1Er_2O_3$–xYb_2O_3 ($x = 0$, 0.2, 0.5, 1 and 2) were prepared by using reagent-grade TeO_2 (99.99%), $PbCl_2$ (99.8%), ZnO (99.99%), Na_2CO_3 (99.99%), Er_2O_3 (99.99%) and Yb_2O_3 (99.99%). The required amounts of raw materials were melted in a platinum crucible at 700–750 °C for an hour under controlled atmosphere. After annealing, samples were polished and cut to the size of 20 mm × 10 mm × 1.5 mm.

The absorption spectra were obtained by a PERKIN-ELMER LAMBDA 900 UV-Vis-NIR spectrophotometer ranging 400–1700 nm with the resolution of 1 nm. Fluorescence spectra were measured on a TRIAX 320 spectrofluorimeter (Jobin-Yvon Corp.) with 808 and 978 nm LD (Coherent Corp.) as excitation sources. Emitted light was focused on to the monochromator and was monitored at the exit slit by a photon-counting R5108 photomultiplier tube (400–1200 nm). The temporal decay curves of the fluorescence signals for the 980 and 1550 nm bands of Er^{3+},