Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Luminescence 117 (2006) 46–52
JOURNAL OF LUMINESCENCE
www.elsevier.com/locate/jlumin

Influence of B_2O_3 to the inhomogeneous broadening and spectroscopic properties of Er^{3+}/Yb^{3+} codoped fluorophosphate glasses

Liyan Zhang[a,b,*], Hongtao Sun[b], Shiqing Xu[a], Kefeng Li[b], Lili Hu[b]

[a]Institute of Optoelectronic Materials and Devices, School of Information Engineering, China Jiliang University, Hangzhou 310018, China
[b]Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Science, Shanghai 201800, China

Received 2 November 2004
Available online 10 May 2005

Abstract

In a three-components fluorophosphate glass system, the introduction of H_3BO_3 brings some valuable influence to the spectroscopic and thermal properties of the glasses. With H_3BO_3 increases from 2 to 20 mol%, Ω_6, $S_{ed4I13/2}$, FWHM, T_g and fluorescence lifetime change from $3.21\times10^{-20}\,cm^2$, $1.77\times10^{-20}\,cm^2$, 45 nm, 480 °C and 8.8 ms to $4.66\times10^{-20}\,cm^2$, $2.11\times10^{-20}\,cm^2$, 50 nm, 541 °C and 7.4 ms, respectively. σ_{abs}, σ_{emi}, FWHM $\times\,\tau_f\times\sigma_{emi}$ has a maximum when H_3BO_3 is 11 mol%. T_g and T_x−T_g increases with H_3BO_3 introduction. Results showed that in fluorophosphate glasses, proper amount of B_2O_3 can be used as a modifier to suppress upconversion and improve spectroscopic properties, broadband property and crystallization stability of the glasses while keeps the fluorescence lifetime relatively high.

PACS: 78.20.−e; 42.70.Ce; 32.70.Cs

Keywords: J–O parameters; Broadband-gain-parameter; Crystallization stability

1. Introduction

Broadband EDFA and ultrashort pulse lasers needed for wavelength-division-multiplexing and soliton transmission system requires gain media with wide and flat gain spectrum over a wide frequency band [1,2]. Although several reports have been published on complicated methods of broadening and flattening the gain spectra of silica-based EDFA [3–5], host material is still an effective way to solve this problem. Glasses with large inhomogeneous broadening and better broadband and flatness properties are promising

*Corresponding author. Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Science, Shanghai 201800, China. Tel.: +86 21 59910994; fax: +86 21 39910393.
E-mail address: jndxzly@hotmail.com (L. Zhang).

0022-2313/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jlumin.2005.04.001

candidates for Er^{3+}-doped lasers and amplifiers [6]. Er^{3+} doped tellurite glass shows high-stimulated emission cross section and broad emission bandwidth in the 1.53 μm region and is considered as one of the most promising materials to realize broadband amplification, but its poor glass thermal stability, strong upconversion and expensive material price make it difficult to practical use [7]. Er^{3+} doped borate bismuth glass also exhibits good broadband properties [8], however, the lifetime of $^4I_{13/2}$ level is relatively low compared with other oxide glasses owing to the large phonon energy (~1400 cm^{-1}) of B–O bond. Er^{3+} doped fluorophosphate glass is another promising host for broadband amplifiers and tunable fiber lasers, many works have been done to broaden the emission band of Er^{3+} in this glass host [6,9]. Because the co-existence of glass formers will induce larger inhomogeneous broadening, thus, in order to make use of the characteristic of broad emission band of B_2O_3 involved glass, proper amount of H_3BO_3 was introduced into a simple fluorophosphate glass system which has three basic components in this study. We found out a balance between the lifetime and FWHM (fluorescence width at half maximum) which can maintain the Er^{3+} doped borate modified fluorophosphate glasses with wide emission band and relatively high fluorescence lifetime. And another advantage of borate involved Er^{3+} glass is the upconversion luminescence is greatly reduced due to the introduction of B–O bonds. No upconversion luminescence was detected in this series glasses.

2. Experiments

Glasses were prepared by mixing appropriate quantities of reagent grade phosphates, fluorides, H_3BO_3, ErF_3 and YbF_3 according to the glass compositions $15Al(PO_3)_3$-$20MgF_2$-xH_3BO_3-$(61-x)BaF_2$-$1ErF_3$-$3YbF_3$ ($x = 2,5,8,11,15,20$ in mol%, which equal to half amount of B_2O_3). Samples devitrified when $x = 0$ or x over 20 mol%. The mixtures were melted at 950–1000 °C in platinum crucible. After refining, melts were cast into a steel mould, annealed to room temperature with a cooling rate 1 °C/5 min, then samples were cut and polished for property measurements.

Absorption spectra were recorded with Perkin–Elmer Lambda 900 UV/VIS/IR Spectrophotometer over a range of 300–2000 nm. Fluorescence spectra were measured with Triax 550 Spectrofluorimeter under 980 nm LD excitation. Fluorescence lifetime of $^4I_{13/2}$ level of Er^{3+} was detected by a HP546800B100-MHz oscilloscope. Refractive indices and densities were obtained through V-prism method and Achimedes method, respectively. All the measurements were taken at room temperature.

3. Results and discussion

3.1. Absorption spectra and Judd– Ofelt analysis

The absorption spectrum is shown in Fig. 1, and each excited levels of Er^{3+} are marked, inset is the enlarged ultraviolet cut-off band graph, which showed a long wavelength shift from 300 to 345 nm with the increasing H_3BO_3. According to [10,11], the electric potential of O^{2-} (3.8 eV) is smaller than that of F^- (4.03 eV), the substitution of H_3BO_3 to BaF_2 narrows the forbidden band of

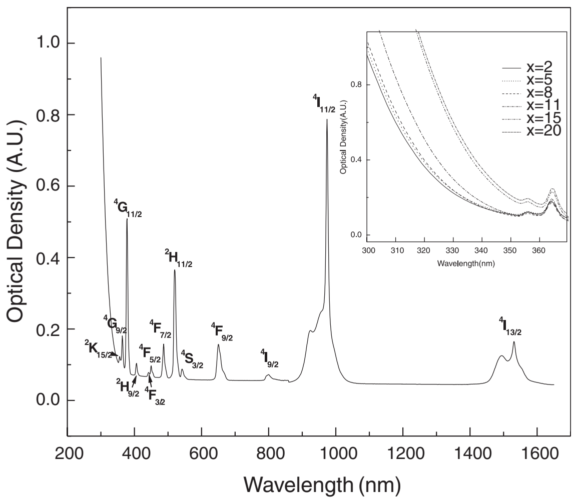

Fig. 1. Absorption spectra of Er^{3+}-doped B_2O_3 modified fluorophosphates glasses, inset is the UV cut-off band of the glasses.