

Tm³⁺/Er³⁺ codoped germanium glasses for photonic applications

Bao-jie Chen and Edwin Yue-Bun Pun

Abstract—Tm³⁺/Er³⁺ codoped sodium magnesium aluminum germanium (NMAG) glasses were prepared and characterized. Broadband near-infrared (NIR) emission in the wavelength range from 1.4 μm to 1.6 μm was observed. The absorption and fluorescence spectra of these glasses were measured and studied. Optical glass waveguides were fabricated using thermal K⁺-Na⁺ ion-exchange process, indicating that NMAG glasses are promising materials for broadband waveguide amplifiers, light sources, and tunable lasers.

Keywords—Broadband emission, Rare earth ions, Ion exchange, optical amplifier

I. Introduction

Increasing demand in network traffic stimulates the development of optical communication systems with broad bandwidth that is beyond the conventional window (1530–1565nm wavelength). Hence, it is essential to develop broadband optical amplifier devices that cover the low-loss wavelength region of silica glass fiber. Rare-earth (RE) ions such as Er³⁺ and Tm³⁺ have attracted much attention due to their unique energy levels, and are often used as the amplification dopants operating in the C/C+L-band (1530–1625 nm) and the S-band (1480–1530 nm) wavelength regions, respectively. Broadband NIR emissions have been obtained in Tm³⁺/Er³⁺ codoped chalcogenide glasses and glass ceramics [1-2], indicating that the co-dopant scheme is an alternate approach to achieving broadband photonic devices. For practical purposes, it is desirable to develop Tm³⁺/Er³⁺ codoped oxide glasses for broadband NIR photonic devices, in order to expand further the fluorescence bandwidth, and utilize fully the entire low loss window in optical fiber.

The Tm³⁺: ³H₄→³F₄ transition suffers severe non-radiative de-excitation when Tm³⁺ ions are doped into conventional oxide glass host materials (for example, silica and phosphate glasses), due to the strong multi-phonon relaxation originating from the high phonon energies of these glasses. Previous investigations have shown that heavy metal oxide glasses are good host materials for achieving efficient Tm³⁺ 1.47μm wavelength emission [3-4], primarily due to their extremely low phonon energies (500–700 cm⁻¹) compared with the phonon energies of other oxide glasses. However, these glasses suffer from medium mechanical strength and large crystallization tendency; hence their applications in the realization of robust device are limited. In this work, Tm³⁺/Er³⁺ codoped NMAG glasses, with good thermal stability, excellent flexibility, and medium-low phonon energy

(<900cm⁻¹), have been prepared and characterized. These glasses are also UV sensitive, and the potential combination of optical waveguides and UV-direct writing gratings will give rise to attractive photonic devices, such as gain-flatten waveguide amplifiers, tunable waveguide lasers, and broadband light sources.

II. Experimental

Tm³⁺/Er³⁺ codoped NMAG glasses were prepared from high-purity Na₂CO₃, MgO, Al₂O₃, and GeO₂ powders according to the host molar composition 23Na₂O-2MgO-22Al₂O₃-53GeO₂. Different doping levels based on the host weight were used. The raw materials were melted following the preparatory procedures described in [5]. The absorption spectra in the wavelength region from 250 nm to 2400 nm were recorded on bulk RE-doped glass samples using a PerkinElmer UV-VIS-NIR Lambda 19 double beam spectrophotometer. After running a background with air as a reference, the spectra were collected with a spectral bandwidth of 2.0 nm at room temperature. The infrared fluorescence spectra were recorded using a Jobin Yvon Fluorolog-3 Spectrophotometer with a near infrared photomultiplier tube (PMT) and a commercial CW Xe-lamp source. The emission decay curves were recorded using the same setup and a flash Xe-lamp source. All measurements were carried out at room temperature.

Thermal K⁺-Na⁺ ion-exchange process was used to fabricate slab and channel optical waveguides in these glasses. The ion-exchange process was performed in pure KNO₃ molten bath at 390°C for several hours, and the refractive index measurements were carried out using a Metricon prism coupler 2010. For the fabrication of channel waveguides, a 150nm-thick high-quality aluminum film was deposited initially on the glass surface using an Edwards Auto 306 thermal evaporator, and 6μm wide windows were opened by wet chemical etching method. After the ion-exchange process, the samples were cooled down to room temperature and the aluminum film was removed. The two end-facets of the waveguides were polished, and the near-field mode patterns were examined using a Hamamatsu vidicon camera.

III. Results and discussion

Figure 1 shows the absorption spectra of Tm³⁺/Er³⁺ (1 wt% : 1 wt%) codoped NMAG glasses, and the emission spectra of Tm³⁺ and Er³⁺ singly doped glasses. All the observed absorption bands corresponding to the electron transitions from the ground state to each specified excited state are indicated. Both the Tm³⁺ and Er³⁺ ions exhibit ground state absorption bands at ~800 nm wavelength, corresponding to the

$\text{Tm}^{3+}: {}^3\text{H}_4 \leftarrow {}^3\text{H}_6$ and the $\text{Er}^{3+}: {}^4\text{I}_{9/2} \leftarrow {}^4\text{I}_{15/2}$ transitions. This absorption is important and significant for obtaining broadband emission using one excitation wavelength. The inset shows the wavelength emissions of Tm^{3+} and Er^{3+} singly doped NMAG glasses.

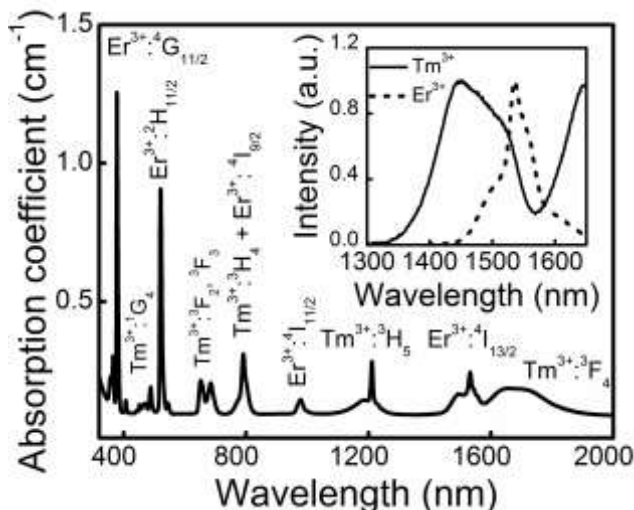


Figure 1 Absorption spectra of $\text{Tm}^{3+}/\text{Er}^{3+}$ codoped NMAG glasses. Inset: Emission spectra of Tm^{3+} - and Er^{3+} - singly doped NMAG glasses under 793nm wavelength excitation, respectively.

Figure 2 shows the NIR emission of $\text{Tm}^{3+}/\text{Er}^{3+}$ codoped NMAG glasses as a function of Tm^{3+} concentration under 793 nm wavelength excitation. The Er^{3+} concentration is fixed at 0.2wt%. A broadband emission, from 1450 nm to 1650 nm wavelength, has been obtained. The characteristic 1.53 μm wavelength emission is from the $\text{Er}^{3+}: {}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ transition, and the emission band locates at 1.47 μm wavelength is from the $\text{Tm}^{3+}: {}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ transition. Both wavelength emissions have been observed in various host materials, and the emission bandwidth depends strongly on the host material. The shorter wavelength side of the 1.53 μm mission increases with

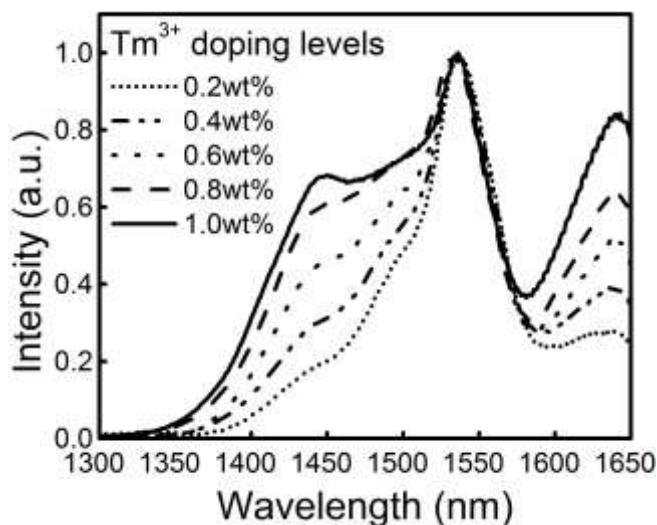


Figure 2 Emission spectra of $\text{Tm}^{3+}/\text{Er}^{3+}$ codoped NMAG glasses as a function of Tm^{3+} concentration under 793 nm wavelength excitation.

increasing Tm^{3+} concentration, and a flat broadband emission with full width at half maximum (FWHM) value of 125 nm is obtained when the $\text{Tm}^{3+}/\text{Er}^{3+}$ concentration ratio reaches $[\text{Tm}]/[\text{Er}]=5$. The $\sim 1.65 \mu\text{m}$ wavelength emission peak recorded is the high-energy edge of the $\text{Tm}^{3+}: {}^3\text{F}_4 \rightarrow {}^3\text{H}_6$ transition (with a peak at $\sim 1.80 \mu\text{m}$ wavelength), and is limited by the response of the NIR PMT. This result implies that the broadband emission characteristics can be maintained for a suitable fixed concentration ratio. Hence, heavy doping can be used to achieve a wide flat gain bandwidth in this wavelength region.

Figure 3 shows the measured lifetime as a function of Tm^{3+} concentration. An average lifetime was determined, because all the decay curves of both the 1.47 and the 1.53 μm wavelength emissions exhibit a slight deviation from single exponential function. With increasing Tm^{3+} concentration, the lifetime of the Tm^{3+} 1.47 μm wavelength emission decreases. The Er^{3+} 1.53 μm wavelength emission lifetime also decreases with increasing Tm^{3+} concentration.

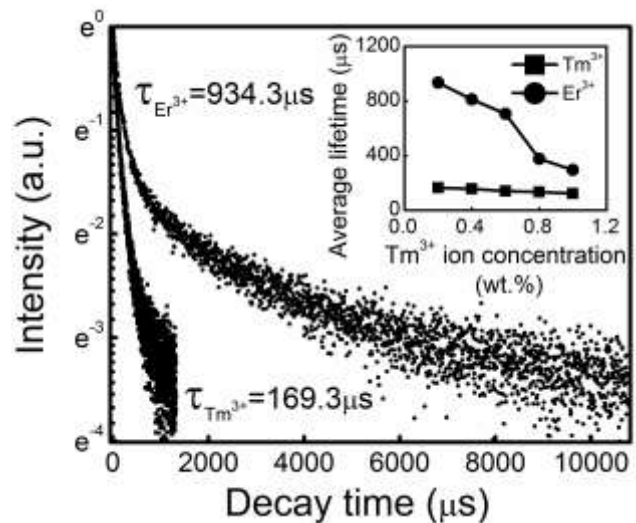


Figure 3 Fluorescence decay curves of $\text{Tm}^{3+}: 1.47 \mu\text{m}$ and $\text{Er}^{3+}: 1.53 \mu\text{m}$ wavelength emissions in $\text{Tm}^{3+}:\text{Er}^{3+}$ (0.2 wt%:0.2 wt%) codoped NMAG glasses. Inset: measured lifetime as a function of Tm^{3+} dopant concentration ($\text{Er}^{3+}: 0.2 \text{ wt}\%$, and Tm^{3+} is 0.2, 0.4, 0.6, 0.8, and 1.0 wt%).

Different possible energy transfer processes have been proposed in reported literatures [6-8]. Figure 4 shows schematically the transition processes, and the details are as follows: (i) Resonant energy transfer (ET) from the $\text{Tm}^{3+}: {}^3\text{H}_4$ state to the $\text{Er}^{3+}: {}^4\text{I}_{9/2}$ state; (ii) Phonon assisted energy transfer from the $\text{Er}^{3+}: {}^4\text{I}_{11/2}$ state to the $\text{Tm}^{3+}: {}^3\text{H}_5$ state; (iii) Quasi-resonant energy transfer from the $\text{Er}^{3+}: {}^4\text{I}_{13/2}$ state to the $\text{Tm}^{3+}: {}^3\text{F}_4$ state with excess energy dissipated in the matrix; (iv) Cross relaxation (CR) process by which the energy is transferred from the $\text{Tm}^{3+}: {}^3\text{H}_4$ excited state to the $\text{Er}^{3+}: {}^4\text{I}_{15/2}$ ground state, leading to a pair of excited $\text{Tm}^{3+}: {}^3\text{F}_4$ and $\text{Er}^{3+}: {}^4\text{I}_{13/2}$ ions; and (v) Energy transfer upconversion process in which excited $\text{Er}^{3+} ({}^4\text{I}_{13/2})$ ions decay non-radiatively to the ground state by exciting Tm^{3+} ions from ${}^3\text{F}_4$ to ${}^3\text{H}_4$. Process (i) is usually ignored in comparison with the energy transfers taking place among lower excited states in the $\text{Tm}^{3+}/\text{Er}^{3+}$ codoped materials. Processes (iii) to (v) can be considered as

quasi-resonant energy transfer with the assistance of phonons because of small energy mismatches. The lifetime decrease of the Tm^{3+} 1.47 μm wavelength emission by the addition of Er^{3+} can be attributed to process (iv), and the lifetime of the Er^{3+} 1.53 μm wavelength emission declines sharply in the presence of Tm^{3+} ions, implying the occurrence of the energy transfer process (iii).

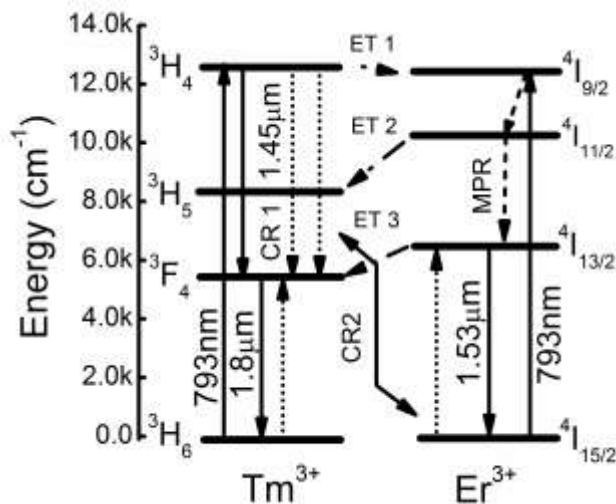


Figure 4 Energy-level diagram showing the NIR luminescence mechanisms of Tm^{3+} and Er^{3+} ions in $\text{Tm}^{3+}/\text{Er}^{3+}$ codoped NMAG glasses under 793 nm wavelength excitation.

In order to demonstrate the practicality of $\text{Tm}^{3+}/\text{Er}^{3+}$ codoped NMAG glasses, optical channel waveguide were fabricated in these glasses using K^+-Na^+ ion exchange process. Single mode waveguides at 1.55 μm wavelength were obtained, and the near-field mode pattern was measured to be 10.5 μm in the horizontal direction and 6.6 μm in the vertical direction, indicating that there can be excellent optical field overlap between the ion-exchanged waveguide and a standard single-mode fiber. Using the cut-back method, the measured propagation loss is estimated to be $\sim 0.35\text{dB/cm}$. The loss can be reduced by using purer materials and improved fabrication method.

iv. Conclusion

Broadband NIR emission in the wavelength range from 1.4 μm to 1.6 μm wavelength has been observed in $\text{Tm}^{3+}/\text{Er}^{3+}$ co-doped NMAG glasses under 793 nm wavelength excitation. The FWHM bandwidth depends on the $\text{Tm}^{3+}/\text{Er}^{3+}$ concentration ratio, and a maximum value of 125 nm has been obtained. The broadband emission characteristics exhibit negligible change with increasing co-dopant concentrations. Cross relaxation processes have been observed and possible energy transfer processes have been proposed. Single-mode channel optical waveguides have been fabricated using thermal K^+-Na^+ ion-exchange process. Ion-exchanged optical waveguides based on low phonon energy UV sensitive $\text{Tm}^{3+}/\text{Er}^{3+}$ co-doped NMAG glasses will lead to the development of novel broadband photonic devices.

Acknowledgment

B.J. Chen is grateful to the City University of Hong Kong for financial support. The work is supported by a CityU Strategic Research Grant project no. 7004059.

References

- [1] Y.S. Xu, D.P. Chen, and W. Wang, et al., "Broadband near-infrared emission in $\text{Er}^{3+}-\text{Tm}^{3+}$ codoped chalcogenide glasses," *Opt. Lett.*, Vol. 33, pp. 2293-2295, 2008.
- [2] D.Q. Chen, Y.S. Wang, F. Bao and Y.L. Yu, "Broadband near-infrared emission from $\text{Tm}^{3+}/\text{Er}^{3+}$ co-doped nanostructured glass ceramics," *J. Appl. Phys.* Vol. 101, 113511, 2007.
- [3] H. Lin, X.Y. Wang, C.M. Li, H.X. Yang, E.Y.B. Pun, and S. Tanabe, "Near-infrared emissions and quantum efficiencies in Tm^{3+} -doped heavy metal gallate glasses for S- and U-band amplifiers and 1.8 μm infrared laser," *J. Lumin.*, Vol. 128, pp. 74–80, 2008.
- [4] D. M. Shi and Q. Y. Zhang, "Enhanced 1.47 μm emission and lowered upconversion of Tm^{3+} -doped gallate-germanium-bismuth-lead glass by codoping rare earths," *J. Appl. Phys.* Vol. 104, 123517, 2008.
- [5] D.L. Yang, E.Y.B. Pun, B.J. Chen, and H. Lin, "Radiative transitions and optical gains in $\text{Er}^{3+}/\text{Yb}^{3+}$ codoped acid-resistant ion exchanged germanate glass channel waveguides," *J. Opt. Soc. Am. B*, Vol. 26(2), pp. 357–363, 2009.
- [6] B. Zhou and E.Y.B. Pun, "Broadband near-infrared photoluminescence and energy transfer in $\text{Tm}^{3+}/\text{Er}^{3+}$ -codoped low phonon energy gallate bismuth lead glasses," *J. Phys. D: Appl. Phys.* Vol. 44, 285404, 2011.
- [7] A.B. de Souzaa, M.T. de Araujoa, and M.V.D. Vermelhoa, et al., "Energy transfer between Tm^{3+} and Er^{3+} ions in a TeO_2 -based glass pumped at diode laser wavelength," *J. Non-Cryst. Solids*, Vol. 353, pp. 94–101, 2007.
- [8] H. Yamauchi, G.S. Murugan and Y. Ohishi, "Optical properties of Er^{3+} and Tm^{3+} ions in a tellurite glass," *J. Appl. Phys.* Vol. 97, 043505, 2005.