400-nm-Bandwidth Emission From a Cr-Doped Glass Fiber

Jian-Cheng Chen, Yen-Sheng Lin, Cheng-Nan Tsai, Kuang-Yao Huang, Chien-Chih Lai, Wei-Zhi Su, Ren-Chin Shr, Fu-Jen Kao, Tao-Yuan Chang, *Senior Member, IEEE*, and Sheng-Lung Huang, *Senior Member, IEEE*

Abstract—Cr^{4+}-doped glass fiber by a laser-heated pedestal growth method is reported. By analyzing the absorption spectra, the transitions of Cr^{3+} and Cr^{4+} in the fibers are identified. With appropriate pumping wavelength and divalent doping concentration, both Cr^{3+} and Cr^{4+} emission bands can be excited simultaneously, and become comparable in their fluorescent intensities. As a result, more than 400-nm-width emission peaked at 1144 nm was generated at room temperature. As much as 12 μW of amplified spontaneous emission was obtained by pumping with a 900-nm Ti:sapphire laser.

Index Terms—Fluorescence spectroscopy, infrared spectroscopy, light sources, optical fiber devices, transition metal compounds.

I. INTRODUCTION

NEAR-INFRARED (NIR) broadband light sources demonstrated in Cr^{4+}-doped crystals, such as forsterite [1]–[3] and YAG [3]–[5], are of great interest for developing tunable solid-state lasers, fiber amplifiers in optical communication systems, and optical coherence tomography (OCT) in biomedics [6]. It is well known that the broad emission of tetrahedrally coordinated Cr^{4+}-doped materials is attributed to the coupling between the electronic levels of 3d electrons with lattice vibrations. The search for Cr^{4+}-activated gain materials has been expanded from crystalline to glass hosts. However, Cr ions are likely to exist in the stable form of +3 oxidation state and hardly found in the tetravalent coordination state in normal glasses. The stable +4 oxidation state of Cr ions has been found in aluminate, alumino–silicate, and gallate glasses [7], although they still suffer from poor emission efficiency [8]. Therefore, the choice of glass compositions for Cr-doped materials is of critical importance, and has been investigated in recent years [7], [9]–[11]. The first Cr^{4+}-doped silica-based optical fiber was fabricated by the modified chemical vapor deposition (MCVD) method [12]. The emission peak was at 1250 nm with

500-nm bandwidth under 860- to 980-nm excitation. However, it can only be operated at low temperature around 77 K. Another study also using the MCVD method found that the fibers doped with aluminum and gallium exhibit a 300-nm emission band of Cr^{4+} ions at 1100 nm at room temperature [13], [14]. After annealing around 1000 °C, the emission spectrum became stronger and transfers to a peak in 790- to 880-nm range with a width of approximately 200 nm, which is attributed to the transition of Cr^{3+}. In our previous study, it was found that both Cr^{3+} and Cr^{4+} ions are coexistent in the YAG-silica diffusion layer of double-clad Cr^{4+}:YAG crystal fiber. In this study, with a well controlled growth condition to make the SiO_2 entirely diffuses into YAG as the core, the Cr^{4+}-doped glass fiber with SiO_2-cladding by the laser-heated pedestal growth method was fabricated. The absorption spectrum by multipeak Gaussian fitting, and the pumping wavelength dependence of emission spectra were investigated at room temperature.

II. EXPERIMENT

A Cr^{4+}:YAG crystal fiber with 66 μm in diameter was grown from a 0.5-mol.% doped Cr^{4+}:YAG with $\langle 111 \rangle$ in crystal orientation and 500 μm $\times$ 500 μm in cross section. The grown crystal fiber was then inserted into a fused-silica capillary tube for redrawing. The silica diffuses into the Cr^{4+}:YAG during redrawing to form the core of the Cr^{4+}-doped glass fiber. The diameters of core and cladding are 90 and 320 μm, respectively. Fig. 1 shows the distributions of fiber compositions, which were measured by an electron probe microanalyzer [(EPMA) JXA-8900R, JEOL]. The composition of the cladding is SiO_2, while the core consists of Y_2O_3, Al_2O_3, and SiO_2. The concentration of Y_2O_3 is about 38 wt.% in the whole core area, while that of Al_2O_3 and SiO_2 is a function of position with average concentrations of 29 and 33 wt.%, respectively.

The absorption spectra were measured using a halogen-tungsten lamp and the signal was detected by spectrometers in visible and NIR ranges separately. The emission spectra were excited using a tunable Ti:sapphire laser (Tsunami-3950, Spectra-Physics) with a tuning range of 750–1000 nm. The signal was collected using a 50/125-μm multimode fiber by butt-coupling.

III. RESULT AND DISCUSSION

Fig. 2(a) shows the three absorption spectra with different concentrations of Cr_2O_3 and CaO. The doping concentrations were controlled by E-gun deposition of Cr_2O_3 and CaO thin-film layers on the circumference of 66-μm Cr^{4+}:YAG crystal fibers. All three samples show similar absorption properties in the visible region with two apparent peaks at 453 and 650 nm, which were also found in silicate glasses [9], [16].

J.-C. Chen, C.-N. Tsai, K.-Y. Huang, W.-Z. Su, R.-C. Shr, and T.-Y. Chang are with the Institute of Electro-Optical Engineering, National Sun Yat-Sen University, Kaohsiung, Taiwan 804, R.O.C.

Y.-S. Lin and C.-C. Lai are with the Graduate Institute of Electro-Optical Engineering, National Taiwan University, Taipei, Taiwan 106, R.O.C.

F.-J. Kao is with the Institute of Biophotonics Engineering, National Yang-Ming University, Taipei, Taiwan 112, R.O.C.

S.-L. Huang is with the Graduate Institute of Electro-Optical Engineering, National Taiwan University, Taipei, Taiwan, R.O.C. He is also with the Department of Electrical Engineering, National Taiwan University, Taipei, Taiwan 106, R.O.C. (e-mail: slhuang@cc.ee.ntu.edu.tw).

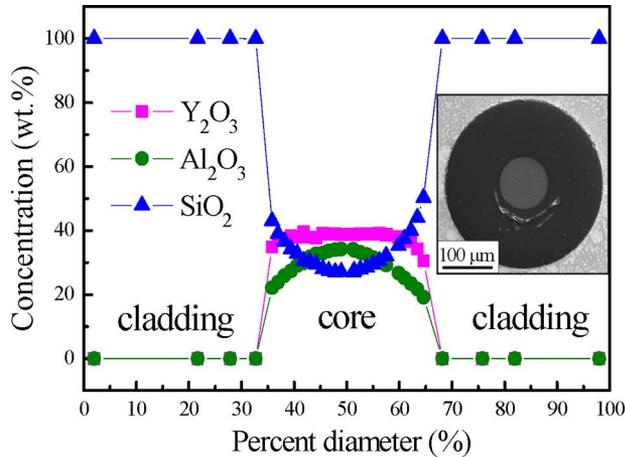Color versions of one or more of the figures in this letter are available online at http://ieeexplore.ieee.org.

Fig. 1. Distributions of host compositions by EPMA measurement. The inset shows the end view of the Cr^{4+}-doped glass fiber.

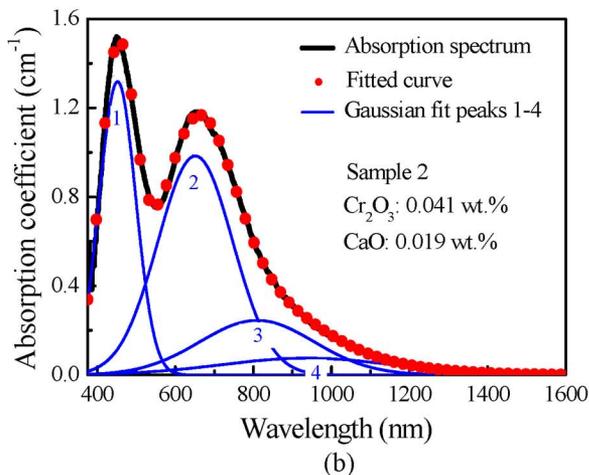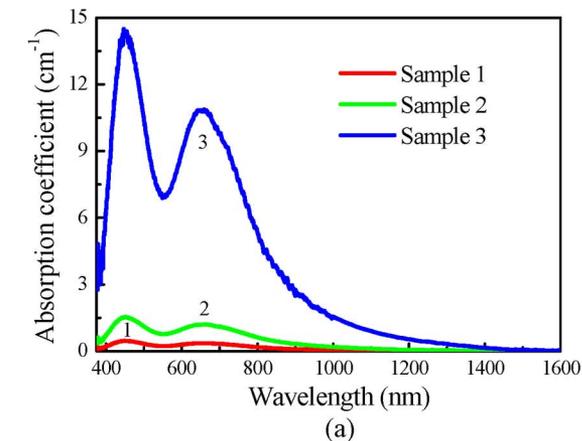Fig. 2. (a) Absorption spectra, and (b) the multipeak Gaussian fitting of Sample 2.

TABLE I
IDENTIFIED TRANSITIONS OF THE THREE SAMPLES USING MULTIPEAK GAUSSIAN FITTING

Sample number	Dopant concentrations (wt.%)	Peak (nm)	Bandwidth (nm)	Oxidation states
1	Cr_2O_3: 0.013 CaO: 0	453 650 810	89 188 300	Cr^{3+} Cr^{3+} Cr^{3+}
2	Cr_2O_3: 0.041 CaO: 0.019	452 651 809 938	90 191 292 437	Cr^{3+} Cr^{3+} Cr^{3+} Cr^{4+}
3	Cr_2O_3: 0.408 CaO: 0.419	453 651 810 982	87 190 293 496	Cr^{3+} Cr^{3+} Cr^{3+} Cr^{4+}

by three Gaussian waveforms with peaks at 453, 650, and 810 nm, which are attributed to the Cr^{3+} ions with transitions of $^4A_2$ to $^4T_1$ and $^4T_2$. As shown in Fig. 2(b), in addition to these three peaks, Sample 2 with a doping of CaO showed an absorption peak at 938 nm with a bandwidth of 437 nm. Similarly, Sample 3 showed an absorption peak at 982 nm with a bandwidth of 496 nm. The broad absorption band from 600 to 1400 nm has been assigned to the transition from Cr^{4+} ion in alumino–silicate glasses [7], [8], [16]. The multipeak fitting for the absorption spectra in these three samples is summarized in Table I. Assuming the Cr ions only exist in +3 and +4 oxidation states, the ratio of Cr^{4+} to total Cr in Samples 2 and 3 can be estimated by comparing the area of absorption peak and concentration of Cr_2O_3 by EPMA measurement. The estimated ratio of Cr^{4+} to total Cr in Samples 2 and 3 are 1.5% and 11.1%, respectively.

As a result of the absorption bands of Cr^{3+} and Cr^{4+} ions overlapped in the NIR region, a tunable Ti : sapphire laser was used to measure the emission spectra. Sample 1 shows a typical Cr^{3+} emission spectrum in silicate glass with a peak around 950 nm when pumping wavelengths are between 750 and 800 nm. The emission bands have a width of approximated 250 nm and a long-wavelength tail up to 1300 nm. The emission spectra of Sample 2 show red shift by increasing the pumping wavelength. It reveals an apparent peak around 1000 nm when pumping wavelengths are between 750 and 800 nm. When longer than 900 nm, the emission peak shifts toward 1150 nm and a broad emission band from 1250 to 1600 nm is generated. It is apparent that it is composed of both the Cr^{3+} and Cr^{4+} emissions. The emission spectra of Sample 3 always showed a peak at 1230 nm with a bandwidth of 340 nm. When pumping at a shorter wavelength, the generation of Cr^{3+} fluorescence is reabsorbed by Cr^{4+} ion and results in the emission at 1230 nm, while for pumping at a longer wavelength, only Cr^{4+} ions can be excited.

Therefore, only Sample 2 generated a combined emission from Cr^{3+} and Cr^{4+} ions. Fig. 3 shows the pumping wavelength dependence of emission peaks and bandwidths of Sample 2. The emission peaks shift from 1008 to 1144 nm, while the bandwidth increases from 268 to 406 nm when increasing pumping wavelength from 750 to 900 nm. It is interesting to note that with a pumping wavelength at 900 nm, both Cr^{3+} and Cr^{4+} emission bands can be excited and become comparable

The corresponding absorption coefficient is almost linearly proportional to the concentration of Cr_2O_3. However, when the concentration of CaO increases to 0.419 wt.%, the absorption spectrum extends to 1400 nm. Here, the multi-Gaussian peaks were fitted to identify the transitions in the Cr^{4+}-doped glass fiber. Sample 1 was made from a pure YAG core only with Cr_2O_3 doping. The absorption spectrum is well fitted
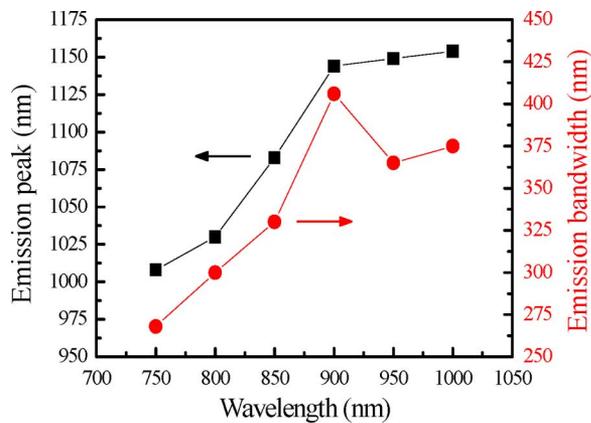
Fig. 3. Excitation wavelength dependence of emission peaks and bandwidths of Sample 2.
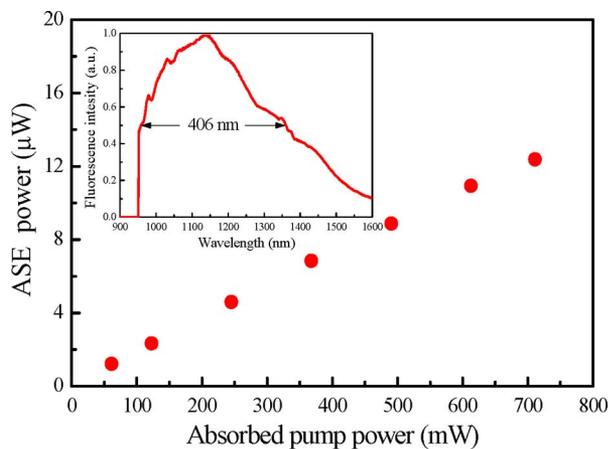

Fig. 4. Measured ASE output power of Sample 2. The inset is the fluorescence spectrum by 900-nm pumping. The pumping light was filtered with a 950-nm long-wavelength-pass filter.

in their intensities to generate the 406-nm broadband emission. In Fig. 4, the power of the amplified spontaneous emission (ASE) was measured. The inset is the corresponding spectrum by using a 950-nm-long wavelength-pass filter to block the pumping power. As much as 12 μW of the ASE power was obtained, which was limited by the output power of the Ti : sapphire laser. It should be noted here that our reflected fluorescence measurement showed that the 3-dB bandwidth of the spontaneous emission was about 483 nm centered around 1050 nm, but its power level was low. According to our simulation, the excited-state absorption cross section is typically less than 20% of the emission cross section. To our knowledge, it is the first report that ASE power with more than 400-nm bandwidth in Cr-doped glass fiber has ever been generated at room temperature. It may be a candidate as a light source for a high-resolution and high-penetration depth OCT system.

IV. CONCLUSION

The red shift of Cr^{3+} fluorescence and blue shift of Cr^{4+} fluorescence in Cr-doped fiber make it possible to form very broadband NIR emission. By the analysis of absorption spectra with multipeak Gaussian fitting, it was found that the absorption peaks at 453, 650, and 810 nm are a transition from Cr^{3+} ions, while that at around 960 nm is the transition from Cr^{4+} ions. With an appropriate pumping wavelength and CaO doping concentration, both Cr^{3+} and Cr^{4+} emission bands can be excited simultaneously, and become comparable in their fluorescent intensities to generate more than 400-nm emission peaked at 1144 nm.

REFERENCES

[1] A. McWilliam, A. A. Lagatsky, C. G. Leburn, P. Fischer, C. T. A. Brown, G. J. Valentine, A. J. Kemp, S. Calvez, D. Burns, M. D. Dawson, M. Pessa, and W. Sibbett, "Low-loss GaInNAs saturable Bragg reflector for mode-locking of a femtosecond Cr^{4+}: Forsterite-laser," *IEEE Photon. Technol. Lett.*, vol. 17, no. 11, pp. 2292–2294, Nov. 2005.

[2] T. Fujii, M. Nagano, and K. Nemoto, "Spectroscopic and laser oscillation characteristics of highly Cr^{4+}-doped forsterite," *IEEE J. Quantum Electron.*, vol. 32, no. 8, pp. 1497–1503, Aug. 1996.

[3] C. R. Pollock, D. B. Barber, J. L. Mass, and S. Markgraf, " Cr^{4+} lasers: Present performance and prospects for new host lattices," *IEEE J. Sel. Topics Quantum Electron.*, vol. 1, no. 1, pp. 62–66, Apr. 1995.

[4] C. Y. Lo, K. Y. Huang, J. C. Chen, S. Y. Tu, and S. L. Huang, "Glass-clad Cr^{4+} : YAG crystal fiber for the generation of superwideband amplified spontaneous emission," *Opt. Lett.*, vol. 29, pp. 439–441, Mar. 2004.

[5] C. Y. Lo, K. Y. Huang, J. C. Chen, C. Y. Chuang, C. C. Lai, S. L. Huang, Y. S. Lin, and P. S. Yeh, "Double-clad Cr^{4+} : YAG crystal fiber amplifier," *Opt. Lett.*, vol. 30, pp. 129–131, Jan. 2005.

[6] M. Rossetti, L. Li, A. Fiore, L. Occhi, C. Velez, S. Mikhrin, and A. Kovsh, "High-power quantum-dot superluminescent diodes with p-doped active region," *IEEE Photon. Technol. Lett.*, vol. 18, no. 18, pp. 1946–1948, Sep. 15, 2006.

[7] T. Murata, M. Torisaka, H. Takebe, and K. Morinaga, "Compositional dependence of the valency state of Cr ions in oxide glasses," *J. Non-Cryst. Solids*, vol. 220, pp. 139–146, 1997.

[8] X. Feng and S. Tanabe, "Spectroscopy and crystal-field analysis for Cr(IV) in alumino-silicate glasses," *Opt. Mater.*, vol. 20, pp. 63–72, 2002.

[9] X. Wu, H. Yuan, W. M. Yen, and B. G. Aitken, "Compositional dependence of the luminescence from Cr^{4+}-doped calcium aluminate glass," *J. Lumin.*, vol. 66&67, pp. 285–289, 1996.

[10] H. Yamazaki and S. Tanabe, "Compositional dependence of fluorescence spectra of Cr^{3+}/Cr^{4+}-doped calcium alumino-silicate glasses for broadband telecommunication," *Jpn. J. Appl. Phys.*, vol. 44, pp. 5011–5013, 2005.

[11] J. C. Chen, K. Y. Huang, C. N. Tsai, Y. S. Lin, C. C. Lai, G. Y. Liu, F. J. Kao, S. L. Huang, C. Y. Lo, Y. S. Lin, and P. Shen, "Composition dependence of the micro-spectroscopy of Cr ions in double-clad Cr:YAG crystal fiber," *J. Appl. Phys.*, vol. 99, pp. 093113–093117, May 2006.

[12] V. Felice, B. Dussardier, J. K. Jones, G. Monnom, and D. B. Ostrowsky, " Cr^{4+}-doped silica optical fibers: Absorption and fluorescence properties," *Eur. Phys. J. AP*, vol. 11, pp. 107–110, 2000.

[13] V. V. Dvoyrin, E. M. Dianov, V. M. Mashinsky, V. B. Neustruev, A. N. Guryanov, A. Y. Laptev, A. A. Umnikov, M. V. Yashkov, and N. S. Vorobev, "Absorption and luminescence properties of Cr^{4+}-doped silica fibers," *Quantum Electron.*, vol. 31, pp. 996–998, 2001.

[14] V. V. Dvoyrin, V. M. Mashinsky, V. B. Neustruev, E. M. Dianov, A. N. Guryanov, and A. A. Umnikov, "Effective room-temperature luminescence in annealed chromium-doped silicate optical fibers," *J. Opt. Soc. Amer. B*, vol. 20, pp. 280–283, Feb. 2003.

[15] V. Felice, B. Dussardier, J. K. Jones, G. Monnom, and D. B. Ostrowsky, "Chromium-doped silica optical fibers: Influence of the core composition on the Cr oxidation states and crystal field," *Opt. Mater.*, vol. 16, pp. 269–277, 2001.

[16] U. Hömmerich, H. Eilers, W. M. Yen, J. S. Hayden, and M. K. Aston, "Near infrared emission at 1.35 μm in Cr doped glass," *J. Lumin.*, vol. 60&61, pp. 119–122, 1994.