Color Variation of the Up-conversion Luminescence in Er^{3+}-Yb^{3+} Co-doped Lead Germanate Glasses and Microsphere Integrated Devices

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***Abstract*—Lead germanate glass samples co-doped with different Er^{3+}/Yb^{3+} concentrations were prepared and the color variation of the up-conversion emissions in these glasses was observed using a 980 nm laser pump. A practical optical integrated device based on Er^{3+}-Yb^{3+} co-doped lead germanate glass microsphere and a special fiber structure, consisting of single mode fiber (SMF), multimode fiber (MMF) and a suspended tri-core hollow fiber (STCHF) is described. As the pump light is coupled into the microsphere from the cores suspended inside the STCHF, the microsphere fixed in the air hole of the STCHF is excited and the up-conversion emissions are observed. Furthermore, when the pump power is increased, the luminescence output color of the microsphere can be readily tuned from yellow to green due to the change of the luminescence intensity ratio of the red to green emissions. This in-fiber microsphere resonator integrated device has the potential to be widely applied in multicolor displays, optical sensors and laser devices owing to its compact structure and excellent performance.**

***Index Terms*—Microsphere, up-conversion, color tuning, hollow fiber, integrated device.**

I. Introduction

In recent years, great interest has been shown in investigating rare earth (RE) doped materials because of their photo-luminescent properties and potential technological applications [1-3]. In particular, RE doped materials show unique up-conversion (UC) luminescence properties, which include large anti-Stokes shifts of several hundred nanometers (>600nm, about 2 eV), sharp emission lines, long UC luminescence lifetimes (~ms), and superior photostability. In early studies, materials based on an inorganic matrix were mainly used in lasers for anti-counterfeiting applications and optical devices [4, 5]. In the past decade, new applications involving the bioimaging of living cells and small animals, biosensors, chemosensors, and other optical fields also have undergone considerable development [6-10]. In addition, the UC luminescence of RE doped materials also plays a significant role in the field of display technology. The UC luminescence color can be efficiently tuned in many ways by changing the ratio of multiple UC emissions bands. For example, by double infrared laser excitation in compound glass systems [11, 12], by tuning the doping activator ions and their concentrations [13, 14], by controlling the size, phase, and surface ligands of lanthanide UC nanophosphors [15-17] or using many other approaches [18, 19].

Many novel RE materials and experimental methods have been proposed to develop UC luminescence technology, but there are a few reports where the UC materials are integrated into optical devices for further practical applications. Recently, multicomponent glass microsphere resonators have attracted significant attention due to their excellent optical properties [20-22]. Such microsphere resonators can be relatively easily integrated within fiber structures due to their small size while still maintaining excellent optical performance [23-25]. In previous work reported by the authors of this article, a form of photonic device which integrates a compound microsphere inside a suspended tri-core hollow fiber (STCHF) structure was described [26]. The temperature sensing properties of the

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device were also characterized in [26]. By choosing an appropriate host material and an effective tuning approach for a compound microsphere located inside an STCHF structure, it is possible to develop a novel optical device which can be widely applied in multicolor displays, optical sensors and lasers.

In this investigation, lead germanate glass samples with different Er^{3+}/Yb^{3+} concentrations co-doped were prepared and the different colors of the UC emissions in these glasses were observed under a 980 nm laser pump. In addition, different Er^{3+} concentrations of lead germanate glass microspheres were prepared and packaged inside an STCHF to form highly integrated optical devices. As the pump power is increased, it is found that the UC luminescence colors can be readily tuned from yellow to green. It is also found that there are differences in the color variation between microspheres with different Er^{3+} concentrations.

II. Theoretical Analysis and Device Fabrication

The Er^{3+}-Yb^{3+} co-doped lead germanate glass samples were prepared using a traditional melt-quenching method, and the details of glass compositions are shown in Table 1. The commercial raw materials PbO, GeO_2, Ga_2O_3, Er_2O_3, and Yb_2O_3 in powder form with 99.99% purity were mixed and melted at 1100°C for 40 min in a muffle furnace. The glass melts were cast into a stainless-steel mold, annealed at 450°C for 3 h and slowly cooled to room temperature.

TABLE I
GLASS LABELS, MOLAR PROPORTIONS OF THE CONSTITUENT CHEMICALS

Glass labels	Chemical composition (mol%)				
	PbO	GeO_2	Ga_2O_3	Er_2O_3	Yb_2O_3
PGG1	45	45	10	0.2	1
PGG2	45	45	10	0.2	2
PGG3	45	45	10	0.2	5
PGG4	45	45	10	0.5	5

The transmission spectra of the Er^{3+}-Yb^{3+} co-doped lead germanate glass was measured using an ultraviolet-visible-NIR spectrophotometer (Lambda-900, PerkinElmer, USA) and the results are shown in Fig. 1. The results indicate that all the lead germanate glasses have high transmittance (up to 80%) in visible range, which is well suited for the emission of strong UC luminescence. There is also a strong absorption peak at 980 nm due to the Yb^{3+} doped ions providing an increase of the absorption cross section at the wavelength. Each absorption peak can be attributed to the electronic transition from the ground-state $^4I_{15/2}$ to the excited state of Er^{3+} as indicated on each peak in Fig. 1. The inset in Figure 1 is an image of the prepared glasses, which indicates that the glasses demonstrate good transparency.

The resulting bulk glasses were ground into powder form and poured into a vertical furnace with an internal gas flow. The powders became molten at high temperature and were transformed into microspheres by surface tension. The relationship between flow rate, temperature and microsphere size was determined based on many repeated experiments. For the microspheres with uniform size of 50 μm used in this experiment, the flow rate and temperature are 2L/min and 800°C, respectively. A more detailed description of the preparation process is described in previous work published by authors of this article [26]. Fig. 2(a) is a microscopic image of the cross-section of the STCHF. Its suspended tri-cores are distributed in an equilateral triangle shape, which means that the microsphere fixed inside STCHF can be fixed in place in a mechanically stable fashion which improves the robustness and reliability of the sensor. The diameter of the air hole is about 80 μm and it provides enough space to allow placement of a microsphere with a radius of 50 μm as shown in Fig. 2(b). As shown in Fig. 2(c) and (d), the microsphere was packaged inside the STCHF using mechanical micro-manipulation allowing the final integrated optical structure to be obtained. Further information regarding the preparation process and optical coupling mechanism of this structure are described in previous work by the authors of this investigation [27].

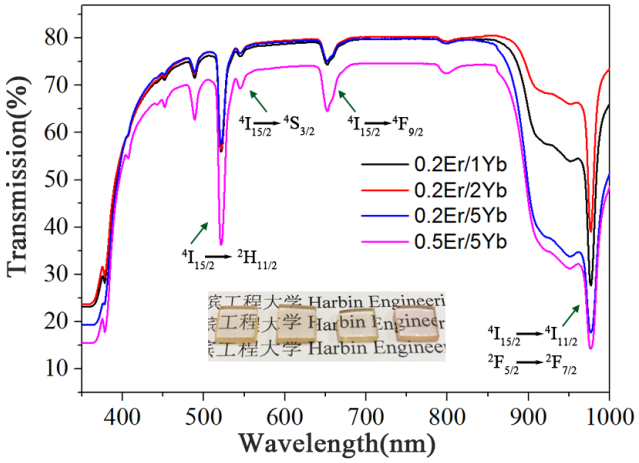

Fig. 1. Transmission spectrum of the Er3+-Yb3+ co-doped lead germanate glass samples, inset: image of the prepared glass samples.

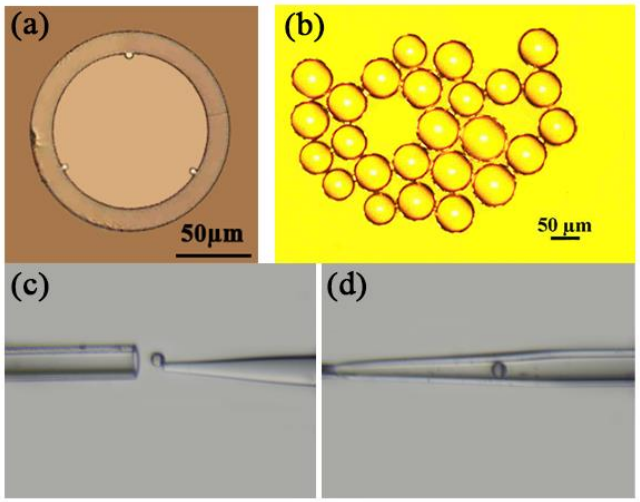

Fig. 2. Microscope images of (a) the cross section of the STCHF, (b) the prepared PGG3 glass microsphere, (c) a microsphere being loaded by an optical half taper fiber and (d) physically encapsulated inside the STCHF following micro- manipulation.

Figure 3 shows the energy level diagram of the Er^{3+} and Yb^{3+} ions under 980 nm laser excitation and the main associated transition mechanisms, including ground-state absorption (GSA), excited-state absorption (ESA) and energy transfer (ET).

The green UC emissions of the Er^{3+} ions may be explained as follows:

(a) GSA: $^4I_{15/2}$ (Er^{3+}) + photon → $^4I_{11/2}$ (Er^{3+});
(b) ET1: $^4I_{15/2}$ (Er^{3+}) + $^2F_{5/2}$ (Yb^{3+}) → $^4I_{11/2}$ (Er^{3+}) + $^2F_{7/2}$ (Yb^{3+});
(c) ET2: $^4I_{11/2}$ (Er^{3+}) + $^2F_{5/2}$ (Yb^{3+}) → $^4F_{7/2}$ (Er^{3+}) + $^2F_{7/2}$ (Yb^{3+});
(d) ESA1: $^4I_{11/2}$ (Er^{3+}) + second photon → $^4F_{7/2}$ (Er^{3+});
(e) $^4F_{7/2}$ (Er^{3+}) → $^2H_{11/2}$ (Er^{3+}) → $^4I_{15/2}$ (Er^{3+});
(f) $^2H_{11/2}$ (Er^{3+}) → $^4S_{3/2}$ (Er^{3+}) → $^4I_{15/2}$ (Er^{3+});

In a similar way, the red UC emission can be understood using the following scheme:

(g) GSA: $^4I_{15/2}$ (Er^{3+}) + photon → $^4I_{11/2}$ (Er^{3+});
(h) ET1: $^4I_{15/2}$ (Er^{3+}) + $^2F_{5/2}$ (Yb^{3+}) → $^4I_{11/2}$ (Er^{3+}) + $^2F_{7/2}$ (Yb^{3+});
(i) $^4I_{11/2}$ (Er^{3+}) → $^4I_{13/2}$ (Er^{3+});
(j) ET3: $^4I_{13/2}$ (Er^{3+}) + $^2F_{5/2}$ (Yb^{3+}) → $^4F_{9/2}$ (Er^{3+}) + $^2F_{7/2}$ (Yb^{3+});
(k) $^4F_{9/2}$ (Er^{3+}) → $^4I_{15/2}$ (Er^{3+}).

By means of such a two-photon-assisted (TPA) process, many Er^{3+} ions transition to the highest excited state from ground state, then by non-radiative decay to the lower excited state and ultimately produce the green emissions at 524 nm, 547 nm and the red emission at 659 nm. There are two cross relaxation (CR) processes between different energy level of Er^{3+} ions. The CR1 is $^2H_{11/2}$ + $^4I_{15/2}$ → $^4I_{9/2}$ + $^4I_{13/2}$ and CR2 is $^4F_{7/2}$ + $^4I_{11/2}$ → $^4F_{9/2}$ + $^4F_{9/2}$. The ET and CR processes mutually influence each other, which may change the particle number distribution of the Er^{3+} energy level which in turn results in a further change in the multiple emission bands intensity.

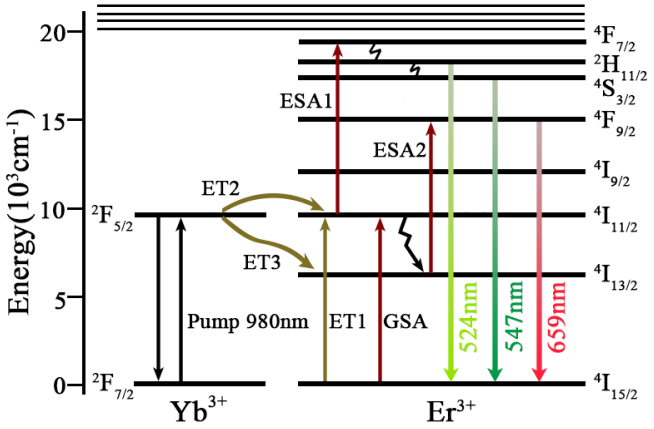

Fig. 3. Energy level diagram of the UC emissions for the Er3+-Yb3+ co-doped lead germanate glass under 980 nm excitation.

III. Experiments and Discussion

Initially, the color variation of the UC luminescence for different Er^{3+}/Yb^{3+} concentrations in the co-doped glasses was observed. Fig. 4 shows the UC luminescence spectra of the PGG1, PGG2 and PGG3 glass samples under the same pump power (0.47 W, 980 nm laser). It was found that the intensity ratio of the red emission to green emission is different for the three glass samples with different Er^{3+}/Yb^{3+} concentration ratios, which results in different UC luminescence colors for the glass samples, as shown in the inset of Fig. 4. It may be affected simultaneously by two factors: One is the ET process between Er^{3+} and Yb^{3+}, and the other is the CR process between Er^{3+} ions. Comparing the UC luminescence spectra of the PGG1 with PGG2 samples, it was possible to conclude that the green emissions take precedence over the red emission when an increase in the Yb^{3+} concentration occurs and the concentration of Er^{3+} remained fixed. This is because, at a lower pump power of 0.47 W, more Er^{3+} ions still populate in the ground state. With an increase in the Yb^{3+} concentration, the ET1 and ET2 processes effectively accelerate and thus more Er^{3+} ions become excited to a higher state and therefore improve the green luminescence emissions. However, if the Yb^{3+} concentration continues to increase, due to overpopulation of electrons in $^4I_{11/2}$ level, the rate of non-radiative relaxation from this level to $^4I_{13/2}$ level will increase and so the ET3 process will send Er^{3+} to the $^4F_{9/2}$ level and finally increase the red luminescence emissions. The CR2 process also becomes significant, which helps to achieve the red color as the dominant emission, which is consistent with the variation between the PGG2 glass and PGG3 glass.

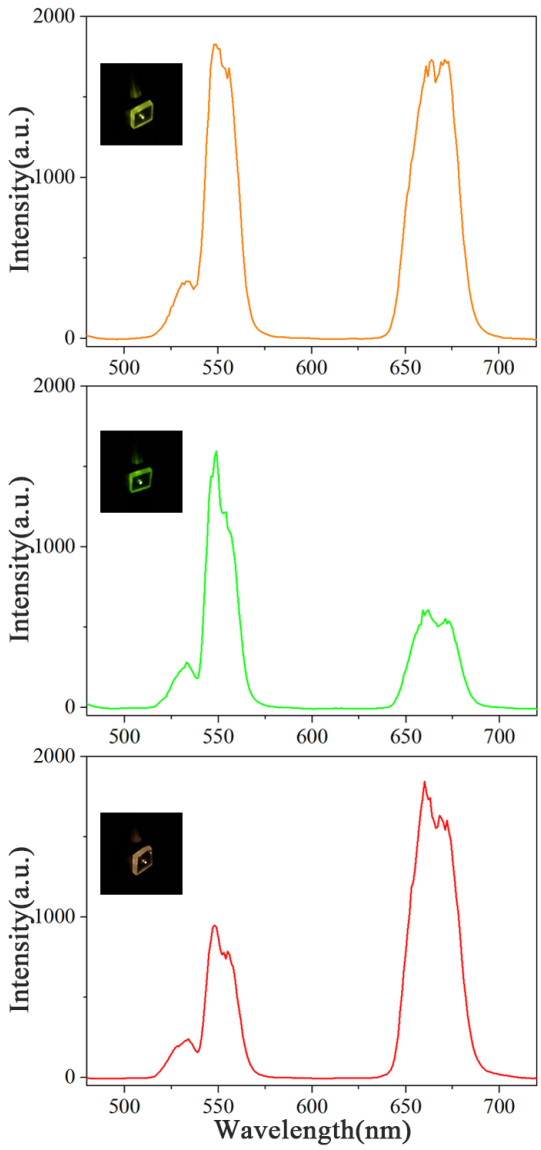

Fig. 4. The UC luminescence spectra of the PGG1, PGG2 and PGG3 glass samples at 0.47 W pump power, inset: the UC luminescence images of three glass samples.

In a subsequent step, the PGG3 glass microsphere was prepared and the color variation observed with increasing the pump power. As shown in Fig. 5(a), the red emission of Er^{3+} is dominant at low pump power, while the green emission is dominant at high power. This can be seen more clearly in Fig. 5(b) as the luminescence intensity data of the emission intensity of the green and red emissions exhibit different growth rates with increasing pump power. When the pump power changes, the Er^{3+} population of the $^4S_{3/2}$ and $^4F_{9/2}$ levels shows a different power dependence, which results the UC color changes [28]. In other words, the output light color is related to the transition probability of the ions occupying the lower excited state $^4I_{11/2}$ [29, 30]. At low pump power, fewer Er^{3+} ions are excited to the $^4I_{13/2}$ state from $^4I_{15/2}$, which results in a relatively low efficiency of the ESA1 process. The majority of the Er^{3+} ions populate the $^4I_{11/2}$ state and relax to the $^4I_{13/2}$ via a non-radiative transition and subsequently transition to the $^4F_{9/2}$ state via the ESA2 process and finally emit a visible red UC fluorescence. Therefore, the luminescence intensity of the red emission is higher than that of the green. When the pump power is high, the green emission of the microsphere is stronger than the red. In addition, there are differences in the color variation due to the different Er^{3+} concentrations of the PGG3 and PGG4 microspheres. Lower pump power is needed to achieve a green luminescence intensity higher than red in higher concentration Er^{3+} doped microspheres. The UC luminescence color of the microspheres can be tuned from yellow to green with an increase in the pump power as shown in the microscope images of the microspheres in Fig. 6 (a) and (c). CIE chromaticity diagrams are a useful way to visualize the color changes in more detail and the CIE chromaticity diagrams are shown in Fig. 6 (b) and (d). It can be seen that if the pump power continues to increase, the UC color is adjusted so that it is closer to pure green. Furthermore, if there is a change of the doping RE ions, for example, $Er^{3+}/Yb^{3+}/Tm^{3+}$ tri-doped, it is possible to achieve a richer color tuning range, confirming the application potential in multicolor displays.

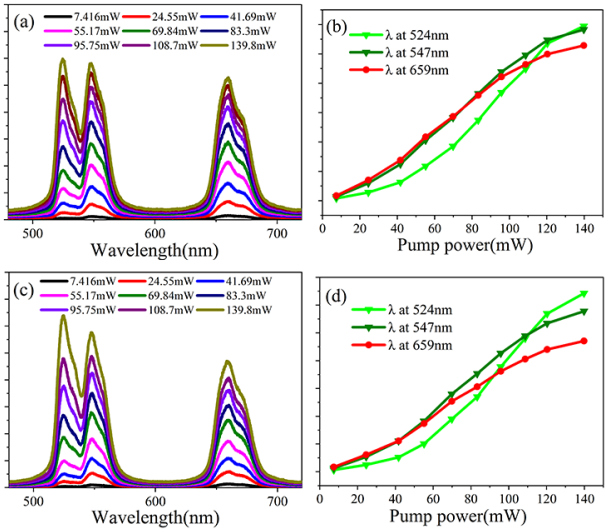

Fig. 5. The UC luminescence spectra of the (a) PGG3 glass microsphere and (c) PGG4 glass microsphere as a function of pump power at room temperature, the luminescence intensity of green emissions at 524 nm and 547 nm and the red emission at 659 nm of the (b) PGG3 glass microsphere and (d) PGG4 glass microsphere as a function of pump power.

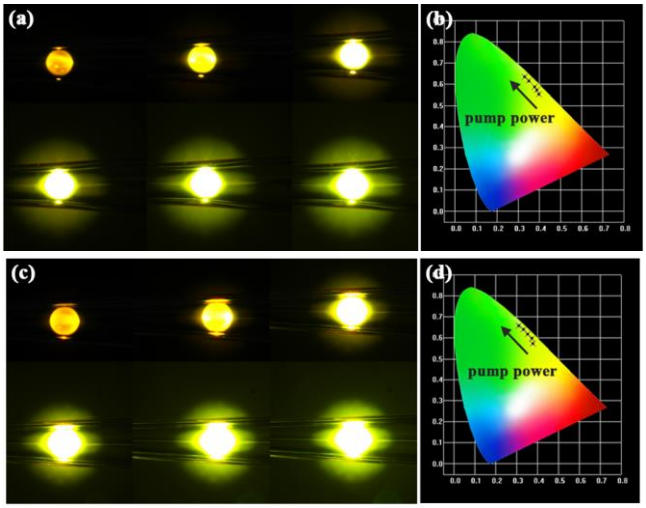

Fig. 6. The microscope images of (a) the PGG3 glass microsphere and (c) the PGG4 glass microsphere with pump power increasing, CIE chromaticity diagram of (b) the PGG3 glass microsphere and (d) the PGG4 glass microsphere at different pump powers.

IV. Conclusion

In summary, several lead germanate glass samples co-doped with different Er^{3+}/Yb^{3+} concentrations were prepared and the color variation of the up-conversion emissions in these glasses was observed when excited using a 980 nm pump laser. The integrated optical device based on structure consisting of a compound microsphere integrated within a STCHF was successfully fabricated and characterized. The Er^{3+}-Yb^{3+} co-doped glass microsphere was encapsulated inside the STCHF and green and red UC emissions were obtained using the 980 nm pump source. It was found that the output UC emission color of the microsphere could be changed from yellow to green by increasing the pump power. In addition, there are differences in the color variation between microspheres with different Er^{3+} concentrations. This integrated device is not disturbed by external environmental changes e.g. vibration, humidity and exhibits excellent performance for use in application areas including optical sensors, multicolor displays as well as many other optical fields.

References

[1] J. Roman *et al.*, "Ion-exchanged Er/Yb waveguide laser at 1.5/spl mu/m pumped by laser diode," *Electronics letters*, vol. 31, no. 16, pp. 1345-1346, 1995.

[2] L. Aigouy, G. Tessier, M. Mortier, and B. Charlot, "Scanning thermal imaging of microelectronic circuits with a fluorescent nanoprobe," *Applied Physics Letters*, vol. 87, no. 18, p. 184105, 2005.

[3] A. Mori, Y. Ohishi, and S. Sudo, "Erbium-doped tellurite glass fibre laser and amplifier," *Electronics Letters*, vol. 33, no. 10, pp. 863-864, 1997.

[4] F. Auzel, "Upconversion and anti-stokes processes with f and d ions in solids," *Chemical reviews*, vol. 104, no. 1, pp. 139-174, 2004.

[5] R. Scheps, "Upconversion laser processes," *Progress in Quantum Electronics*, vol. 20, no. 4, pp. 271-358, 1996.

[6] J. Zhou, Z. Liu, and F. Li, "Upconversion nanophosphors for small-animal imaging," *Chemical Society Reviews*, vol. 41, no. 3, pp. 1323-1349, 2012.

[7] F. Wang, D. Banerjee, Y. Liu, X. Chen, and X. Liu, "Upconversion nanoparticles in biological labeling, imaging, and therapy," *Analyst*, vol. 135, no. 8, pp. 1839-1854, 2010.

[8] D. K. Chatterjee, M. K. Gnanasammandhan, and Y. Zhang, "Small upconverting fluorescent nanoparticles for biomedical applications," *Small*, vol. 6, no. 24, pp. 2781-2795, 2010.
[9] H. S. Mader, P. Kele, S. M. Saleh, and O. S. Wolfbeis, "Upconverting luminescent nanoparticles for use in bioconjugation and bioimaging," *Current opinion in chemical biology*, vol. 14, no. 5, pp. 582-596, 2010.
[10] L. Y. Ang, M. E. Lim, L. C. Ong, and Y. Zhang, "Applications of upconversion nanoparticles in imaging, detection and therapy," *Nanomedicine*, vol. 6, no. 7, pp. 1273-1288, 2011.
[11] E. Downing, L. Hesselink, J. Ralston, and R. Macfarlane, "A three-color, solid-state, three-dimensional display," *Science*, vol. 273, no. 5279, pp. 1185-1189, 1996.
[12] D. Yeh, R. Petrin, W. Sibley, V. Madigou, J. Adam, and M. Suscavage, "Energy transfer between Er 3+ and Tm 3+ ions in a barium fluoride–thorium fluoride glass," *Physical Review B*, vol. 39, no. 1, p. 80, 1989.
[13] H. Gong, D. Yang, X. Zhao, E. Y. B. Pun, and H. Lin, "Upconversion color tunability and white light generation in Tm3+/Ho3+/Yb3+ doped aluminum germanate glasses," *Optical Materials*, vol. 32, no. 4, pp. 554-559, 2010.
[14] N. Wang, X. Zhao, C. Li, E. Pun, and H. Lin, "Upconversion and color tunability in Tm3+/Ho3+/Yb3+ doped low phonon energy bismuth tellurite glasses," *Journal of Luminescence*, vol. 130, no. 6, pp. 1044-1047, 2010.
[15] S. Schietinger, L. d. S. Menezes, B. r. Lauritzen, and O. Benson, "Observation of size dependence in multicolor upconversion in single Yb3+, Er3+ codoped NaYF4 nanocrystals," *Nano letters*, vol. 9, no. 6, pp. 2477-2481, 2009.
[16] D. Yuan, M. C. Tan, R. E. Riman, and G. M. Chow, "Comprehensive study on the size effects of the optical properties of NaYF4: Yb, Er nanocrystals," *The Journal of Physical Chemistry C*, vol. 117, no. 25, pp. 13297-13304, 2013.
[17] D. Yuan, G. S. Yi, and G. M. Chow, "Effects of size and surface on luminescence properties of submicron upconversion NaYF 4: Yb, Er particles," *Journal of Materials Research*, vol. 24, no. 6, pp. 2042-2050, 2009.
[18] Q. Su *et al.*, "The effect of surface coating on energy migration-mediated upconversion," *Journal of the American Chemical Society*, vol. 134, no. 51, pp. 20849-20857, 2012.
[19] H. Wen *et al.*, "Upconverting near - infrared light through energy management in core – shell – shell nanoparticles," *Angewandte Chemie International Edition*, vol. 52, no. 50, pp. 13419-13423, 2013.
[20] T. Kishi, T. Kumagai, S. Shibuya, F. Prudenzano, T. Yano, and S. Shibata, "Quasi-single mode laser output from a terrace structure added on a Nd 3+-doped tellurite-glass microsphere prepared using localized laser heating," *Optics express*, vol. 23, no. 16, pp. 20629-20635, 2015.
[21] D. H. Broaddus, M. A. Foster, I. H. Agha, J. T. Robinson, M. Lipson, and A. L. Gaeta, "Silicon-waveguide-coupled high-Q chalcogenide microspheres," *Optics express*, vol. 17, no. 8, pp. 5998-6003, 2009.
[22] D. Ristić *et al.*, "Photoluminescence and lasing in whispering gallery mode glass microspherical resonators," *Journal of Luminescence*, vol. 170, pp. 755-760, 2016.
[23] K. Kosma, G. Zito, K. Schuster, and S. Pissadakis, "Whispering gallery mode microsphere resonator integrated inside a microstructured optical fiber," *Optics letters*, vol. 38, no. 8, pp. 1301-1303, 2013.
[24] R. Wang, M. Fraser, J. Li, X. Qiao, and A. Wang, "Integrated in-fiber coupler for microsphere whispering-gallery modes resonator excitation," *Optics letters*, vol. 40, no. 3, pp. 308-311, 2015.
[25] X. Zhang *et al.*, "Theoretical aspects and sensing demonstrations of cone-shaped inwall capillary-based microsphere resonators," *Photonics Research*, vol. 5, no. 5, pp. 516-520, 2017.
[26] M. Zhang *et al.*, "In-fiber temperature sensor based on green up-conversion luminescence in an Er 3+-Yb 3+ co-doped tellurite glass microsphere," *Optics Letters*, vol. 44, no. 13, pp. 3214-3217, 2019.
[27] M. Zhang *et al.*, "In-fiber whispering-gallery mode microsphere resonator-based integrated device," *Optics Letters*, vol. 43, no. 16, pp. 3961-3964, 2018/08/15 2018.
[28] M. Pollnau, D. R. Gamelin, S. Lüthi, H. Güdel, and M. P. Hehlen, "Power dependence of upconversion luminescence in lanthanide and transition-metal-ion systems," *Physical Review B*, vol. 61, no. 5, p. 3337, 2000.
[29] J. L. Ferrari, K. de Oliveira Lima, E. Pecoraro, R. A. Ferreira, L. D. Carlos, and R. R. Gonçalves, "Color tunability of intense upconversion emission from Er 3+–Yb 3+ co-doped SiO 2–Ta 2 O 5 glass ceramic planar waveguides," *Journal of Materials Chemistry*, vol. 22, no. 19, pp. 9901-9908, 2012.
[30] C. Ming, F. Song, and X. Ren, "Color variety of up-conversion emission of Er3+/Yb3+ co-doped phosphate glass ceramics," *Current Applied Physics*, vol. 13, no. 2, pp. 351-354, 2013.