Yb^{3+}-Yb^{3+} Cooperative Upconversion in Oxyfluoride Glass and Glass Ceramics

Xin Wang [1], Wenhao Li [1], Shunbin Wang [1], Shijie Jia [1], Yongkang Dong [2], Gilberto Brambilla [3,*] and Pengfei Wang [1,4,*]

[1]*Key Laboratory of In-fiber Integrated Optics of Ministry of Education, College of Science, Harbin Engineering University, Harbin 150001, China*

[2] *National Key Laboratory of Science and Technology on Tunable Laser, Harbin Institute of Technology, Harbin 150001, China*

[3] *Optoelectronics Research Centre, University of Southampton, Southampton SO17 1BJ, United Kingdom*

[4] *Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China*

*gilberto@soton.ac.uk

*pengfei.wang@tudublin.ie

Abstract:

Yb^{3+}-doped oxyfluoride glasses and glass ceramics containing $KZnF_3$ nanocrystals were obtained by melt-quenching. Under excitation of a 980 nm laser, a strong blue emission from Yb^{3+}-Yb^{3+} cooperative upconversion was observed in the glass sample, which increased by five times in glass ceramics after heat treatment for 20 hours. The photoluminescence mechanism and sample properties were investigated by X-ray diffraction, transmission electron microscopy, fluorescent lifetime, absorption and emission spectra. The size of $KZnF_3$ nanocrystals is in the range 5 nm to 20 nm, making the glass ceramic samples highly transparent. The STEM-EDS measurements indicate that the distribution of Yb is consistent with that of the $KZnF_3$ nanocrystals. Fluroide phase

provides a low-phonon-energy environment for Yb^{3+}-Yb^{3+} ion pairs, which facilitates an intense fluorescent blue emission in the $KZnF_3$ crystal lattice. Both theoretical and experimental results demonstrate that Yb^{3+}-doped oxyfluoride glasses and glass ceramics containing $KZnF_3$ nanocrystals are promising materials for blue upconversion emission.

Keywords: Glass ceramics; $KZnF_3$ nanocrystal; cooperative upconversion.

Introduction

Because of their unique upconversion luminescence in the ultraviolet (UV) visible and near-infrared (NIR) spectral ranges, rare earth doped materials have been investigated for applications in many fields, such as illumination display, bioluminescent labeling, optical communication, and lasers[1-5]. Upconversion luminescence is a process of converting two or more low-energy photons into a high-energy photon (usually from infrared to visible or ultraviolet) [6,7]. The occurrence of such multiphoton process relies on lanthanide ions with abundant electronic energy levels. The characteristic emission spectra of lanthanide ions are distributed over a wide spectral region ranging from the infrared to the UV, and include Tm^{3+} and Yb^{3+} ions that can emit blue light. Blue light can be used in fields such as optical recording, fluorescent marking, and optical measurements[8-10].

Most of the studies on blue upconversion luminescence focused on Tm^{3+}-doped materials, and, less frequently, on Yb^{3+}-doped upconversion materials[11-13]. In 1989, Nguyen reported blue upconversion luminescence of Tm^{3+} in YLF crystals[14]. In 1991, Hirao et al. reported Tm^{3+} upconversion luminescence in fluoroaluminate glasses[15]. As Tm^{3+} has multiple energy levels, the photon energy absorbed from a single excitation source is distributed over many energy levels, so that a part of the energy cannot be emitted in the form of blue fluorescence[16]. Yb^{3+} ions have a simple two-level structure, and in the upconversion luminescence process, the near-infrared photons absorbed by Yb^{3+} can be converted into blue fluorescence emission with almost 100% efficiency. The blue upconversion luminescence of Yb^{3+} has been reported by Xu and Malinowski et al[17,18]. It is well known that there are many materials that can achieve upconversion luminescence such as glasses, crystals, phosphors and organic dyes. Glass materials usually have high phonon energy, and the up-conversion luminescence intensity is limited. However, the fabrication of single crystals is difficult, and polycrystalline materials are affected by intergranular scattering[19-22]. Glass-ceramics combine the advantages of low phonon energy observed in crystals and of easy manufacturing found

in glass materials, providing a new research direction for up-conversion luminescence[23-25].

In this paper, we theoretically and experimentally demonstrated Yb^{3+}-doped fluorosilicate glass ceramics (GCs) containing $KZnF_3$ nanocrystals. These GCs have both the advantages of oxide glasses, such as good chemical stability and mechanical behavior, and of fluoride crystals, such as low phonon energy and strong crystal field. Under the excitation of a 980 nm laser, intense blue emission was obtained in the glass sample, and the intensity increased five times after thermal treatment.

Theory and experiments

In the past, Yb^{3+}-doped fluorosilicate glasses have shown efficient upconversion, indicating that the structure of the fluorosilicate glass may provide a local low-phonon-energy environment for the Yb^{3+} luminescence, similar to that observed in nanocrystals[26]. To investigate the structure of such fluorosilicate glass, a customized molecular dynamics (MD) simulation was utilized to predict the structural evolution of a $55SiO_2$-22.5KF-$22.5ZnF_2$ glass system. A cubic cell containing 3524 atoms was defined in the simulation model and was subjected to periodic boundary conditions. The cubic cell had a volume of $(24.25\ Å)^3$ based on the experimental density of 2.992 g/cm^{-3}. A Born-Mayer interatomic pair potential was adopted for the following simulation:

$$\Phi_{ij}(r) = \frac{e^2}{4\pi\varepsilon_0}\frac{Z_i Z_j}{r} + B_{ij}\exp\left(-\frac{r}{\rho_{ij}}\right) \quad (1)$$

where r is the interatomic distance between atoms i and j, Z_i and Z_j the effective charges, and B_{ij} and ρ_{ij} the repulsive constant and the softness parameter, respectively. Φ_{ij} is the interaction energy of atoms i and j, representing the Coulombic interaction and short-range repulsion, respectively. For each cation-cation pair, the value of B was fixed at zero. The Coulombic interactions were calculated using the Ewald summation method. To avoid atoms overlapping, the initial atomic coordinates were randomly distributed with constraints between ion pairs. The time step for this simulation was set at 1 fs. The glass was firstly equilibrated at 4000 K with 20.000 time steps, then quenched to 293 K with 100,000 time steps. A final relaxation, with 20,000 time steps, was carried out at room temperature (293 K). The glass structural information, such as coordination number and bond length, was extracted from the last configuration of the simulated model.

Figure 1 (a-d) shows the predicted distributions of silicon (Si), Potassium (K), Zinc (Zn) and Fluorine (F). While Si exhibits a homogeneous distribution, K, Zn and F are heterogeneously

distributed inside the glass matrix. The size of the F-rich regions are circa 1 nm, and probably originated in the melt, starting from a liquid–liquid phase separation.

All glass samples were prepared by traditional high temperature casting. The composition of the glass was $55SiO_2$-22.5KF-$22.5ZnF_2$ (mol%) and $x YbF_3$(x=0.3, 0.5, 0.7, 0.9 mol%) powders were added and stirred evenly[27]. A total of 30g of high purity (99.99%) powers of SiO_2, KF, ZnF_2 and YbF_3 powders were mixed and melted in a closed platinum rhodium crucible at 1400 ˚C for 20 mins. The glass melt was then poured at room temperature on a copper plate and another copper plate was pressed against the glass melt to form a transparent precursor glass (PG). The glass samples were then annealed at 450 ˚C for 3 hours to eliminate any internal stress. The PG underwent heat treatment at 540 ˚C for 5, 10, 20 hours to turn into GCs containing $KZnF_3$ nanocrystals. In order to make further optical measurements on the glass and GC samples, the sample surfaces were polished. The absorption and fluorescence spectra of the glass samples were measured by a UV/VIS/NIR spectrophotometer (Lambda-900, PerkinElmer, USA) and a fluorescence spectrometer (FLS920, Edinburgh Instruments, UK). The presence of crystalline species was confirmed by X-ray diffraction (XRD) using a D8 advance X-ray diffractometer (Bruker, Faellanden, Switzerland) with Cu-Kα irradiation. The morphology, size and elemental distribution of nanocrystals were measured by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). All the PG and GC samples were cut into 1cm x 1 cm with the thickness of 1.3 mm.

Result and discussion

Figure 2 shows the optical absorption spectra of undoped and Yb^{3+} doped fluorosilicate glass and GC (540˚C-10h) samples. Compared to the undoped sample, the Yb^{3+} doped glass and glass ceramic samples has an obvious absorption peak located at around 980 nm, which could be attributed to the Yb^{3+}: $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition. No other absorption peak was observed in the spectra, indicating that no significant amount of other rare earth impurities was present in the glass or GC samples. In addition, it can be found the illustration that glass and glass ceramic samples have high transmittance in the visible light region, and the scattering phenomenon caused by nanocrystals in glass ceramic samples leads to a significant decrease in transmittance of glass ceramic samples at 400nm.

Figure 3 (a) and (b) show photographs of the Yb^{3+}-doped glass and GC samples with $KZnF_3$ nanocrystals. Under the excitation of a 980 nm laser, the Yb^{3+} doped glass and glass ceramic sample exhibited an intense blue luminescence, as shown in Fig. 3 (a). Both glass and GC samples have high transmittance in the visible as shown in Fig. 3 (b).

Figure 4 (a) and (b) show the emission spectra of *x*Yb^{3+} (in mol%, *x*=0.3, 0.5, 0.7, 0.9) doped glasses in the visible region and relationship between the concentration and cooperative upconversion luminescence intensity under the excitation of a 980 nm laser, respectively. With increasing concentrations of Yb^{3+}, the intensity of upconversion luminescence at 480nm increases and reaches the maximum value at the Yb^{3+} concentration of 0.7 mol% before decreasing. This result can be explained by Yb^{3+} concentration quenching.

Figure 5 (a) shows XRD patterns of the glass and glass-ceramic after heat treatment at 540 ˚C for 20 hours. In the XRD spectrum, the glass samples show the typical diffused peaks commonly observed in amorphous glass materials. On the contrary, the glass-ceramic samples show multiple narrow diffraction peaks at specific positions on the background baseline of the glass broad peaks. A comparison with standard cards (89-4110) allowed to attribute these characteristic peaks to the $KZnF_3$ crystal. This indicates that $KZnF_3$ crystals are indeed formed in the matrix glass after heat treatment, consistently with the molecular dynamic simulations. Fig. 5 (b) shows the HRTEM patterns of the GC samples. $KZnF_3$ nanocrystals are uniformly distributed in the glass, with a size from 5 to 20 nm. The inter-planar distance, indicated in Fig. 5 (b), is 0.3 nm, which roughly corresponds to the $KZnF_3$ crystal plane (110).

Figure 6 (a) shows the emission spectra of Yb^{3+} doped glass and GC samples with different heat treatment times. Under the excitation at 980 nm, the GC upconversion luminescence intensity is

higher than that of the glass. For the heat treatment time increased from 0 hour to 20 hours, the luminescence intensity increased monotonously. When the heat treatment times increased over 20 hours, the transmittance of GC sample decreased Significantly. So, 20 hours is the best heat treatment time for this GC sample. This result can be explained by the formation of GC with $KZnF_3$ nanocrystals from the glass sample after heat treatment. On one hand, the concentration of most of Yb^{3+} ions in the $KZnF_3$ nanocrystal lattice results in a reduced average distance between the Yb^{3+} ions, which is conducive to the formation for Yb^{3+} ion pairs and the improvement of cooperative upconversion efficiency. On the other hand, the glass sample exhibits a high probability of non-radiative decay, thus the emission intensity in the PG is weak. Compared to PG sample, the intensity of upconversion emission in GC heat treated for 20 hours increased 5 times. The strong GC crystal field results in a low probability of non-radiative decay, thus a luminescence intensity enhancement, consistent with the decay curves shown in Fig. 6 (b).

To further confirm that the Yb^{3+} ions entered the crystal lattice, the dopant distributions were studied by high angle annular dark field STEM (HAADF-STEM) and scanning TEM with an energy-dispersive spectrometer (STEM-EDS), as shown in Figure 7. The mapping analysis shows that the nanocrystals are rich in K (Fig. 7c), F (Fig. 7d) and Zn (Fig. 7g), and, more importantly, the distribution of Yb (Fig. 7b) is consistent with that of the nanocrystals, proving that most Yb^{3+} ions enter the nanocrystal lattice. Fig. 7 (e) shows a schematic of the $KZnF_3$ structure: Yb^{3+} ions can substitute Zn with 6 coordination in the crystal lattice due to their similar radii (86.8 pm for Yb^{3+} versus 74 pm for Zn^{2+}), and located YbF_6 octahedra. These measurements are in good agreement with the theoretical prediction summarized in Fig. 1.

To investigate the mechanism behind the Yb^{3+} cooperative upconversion emission, the pump power

dependence was measured and is summarized in Figure 8 (a). When the pump power increased, the intensity of the upconversion emission grew monotonously. The relationship between the upconversion intensity (I_{uc}) and the pump power (I_{pump}) can be fitted by the polynomial: $I_{uc} \propto (I_{pump})^n$, where n represents the number of absorbed photon numbers per emitted photon. The inset of Fig. 8 shows that the fitting curve has n=1.96 [28], consistent with the model that assumes two Yb^{3+} ions absorbing two 980 nm photons and emitting a single photon in the visible[29]. The blue emission of Yb^{3+} ion pairs in cooperative upconversion process could result by radiative relaxation of the excited Yb^{3+}-Yb^{3+} ($^2F_{5/2}$ $^2F_{5/2}$) ion pairs to the ground state Yb^{3+}-Yb^{3+} ($^2F_{7/2}$ $^2F_{7/2}$) ion pairs.

Conclusion

In conclusion, intense blue emission was observed in fluorosilicate glass doped only with Yb^{3+} under the excitation at 980nm. After thermal treatment, a transparent GC containing $KZnF_3$ nanocrystals was obtained and the blue luminescence intensity increased five times due to large number of Yb^{3+} ions enter the nanocrystals to form Yb^{3+} ion pairs. TEM images showed that the distribution of nanocrystals was uniform with sizes of ~5-20 nm. An upconversion peak centered at 480nm was observed and explained by a cooperative upconversion mechanism of two photons based on Yb^{3+}-Yb^{3+} ion pairs. In order to obtain brighter upconversion luminescence, the emission intensity was enhanced by changing the doping concentration of Yb^{3+} and by precipitating $KZnF_3$ nanocrystal by heat treatment. The material shows potential applications in various fields, such as high-power lasers, laser illumination, displays and biosensors.

Acknowledgments:

This work was supported by the National Key program of National Natural Science Foundation of China (NSFC) under grant 61935006, the fundamental research funds for the central universities

(HEUCFG201841), Open Fund of the State Key Laboratory on Integrated Optoelectronics (IOSKL2016KF03), the 111 project (B13015) to the Harbin Engineering University and the Ph.D. Student Research and Innovation Fund of the Fundamental Research Funds for the Central Universities (3072019GIP2518).

References:

[1] Liu L, Lu K, Xu L, Tang D, Liu C, Shahzad, Shahzad MK, Dong Y, Khan F, Zhao E, Li H. Highly efficient upconversion luminescence of Er heavily doped nanocrystals through 1530 nm excitation. Opt Lett. (2019); 44(3), 711-714.

[2] Zhao Z, Shen J, Wang M, Simultaneous imaging of latent fingerprint and quantification of nicotine residue by NaYF4: Yb/Tm upconversion nanoparticles. Nanotechnology, (2020), 31(14): 145504.

[3] Zheng K, Zhao D, Zhang D, Liu N, Qin W. Ultraviolet upconversion fluorescence of $Er3^{+}$ induced by 1560 nm laser excitation. *Opt Lett.* 2010;35(14):2442-2444.

[4] El-Agmy RM. Upconversion CW laser at 284 nm in a Nd:YAG-pumped double-cladding thulium-doped ZBLAN fiber laser. *Laser Phys.* 2008;18(6):803.

[5] Chen GY, Liu Y, Zhang YG, Somesfalean G, Zhang ZG, Sun Q, Wang FP. Bright white upconversion luminescence in rare-earth-ion-doped Y_2O_3 nanocrystals. *Appl Phys Lett.* 2007;91(13):133103.

[6] Chen D, Wang Y, Yu Y, Huang P. Intense ultraviolet upconversion luminescence from Tm^{3+}/Yb^{3+}:β-YF_3 nanocrystals embedded glass ceramic. *Appl Phys Lett.* 2007;91(5): 051920.

[7] Chen D, Wang Y, Zheng K, Guo T, Yu Y, Huang P. Bright upconversion white light emission in transparent glass ceramic embedding $Tm^{3+}/Er^{3+}/Yb^{3+}$:β-YF_3 nanocrystals. *Appl*

Phys Lett. 2007;91(25):251903.

[8] Vetrone F, Mahalingam V, Capobianco JA. Near-infrared-to-blue upconversion in colloidal $BaYF_5$:Tm^{3+}, Yb^{3+} nanocrystals. *Chem Mater.* 2009;21(9):1847-1851.

[9] Mehrabani S, Armani AM. Blue upconversion laser based on thulium-doped silica microcavity. *Opt Lett.* 2013;38(21): 4346-4349.

[10] Gouveia-Neto AS, da Costa EB, dos Santos PV, Bueno LA, Ribeiro SJL. Sensitized thulium blue upconversion emission in Nd^{3+}/Tm^{3+}/Yb^{3+} triply doped lead and cadmium germanate glass excited around 800 nm. *J Appl Phys.* 2003;94(9):5678-5681.

[11] Zhao X, Suo H, Zhang Z, Guo, C. Upconverting CeO2: Yb3+/Tm3+ hollow nanospheres for photo-thermal sterilization and deep-tissue imaging in the first biological window. Ceramics International, (2019). 45(17), 21910-21916.

[12] Jacquier B, Linare`s C, Mahiou R, Adam JL, De´noue E, Lucas J. Efficient blue upconversion in Tm^{3+} and Pr^{3+} doped BIGaZYbTZr glasses. *J Lumin.* 1994;60-61:175-178.

[13] Martín IR, Méndez-Ramos J, Rodríguez VD, Romero JJ, García-Solé J. Increase of the 800 nm excited Tm^{3+} blue upconversion emission in fluoroindate glasses by codoping with Yb^{3+} ions. *Opt Mater.* 2003;22(4):327-333.

[14] Nguyen DC, Faulkner GE, Dulick M. Blue-green (450-nm) upconversion Tm^{3+}:YLF laser. *Appl Opt.* 1989;28(17): 3553-3555.

[15] Hirao K, Tanabe S, Kishimoto S, Tamai K, Soga N. UV and blue upconversion in Tm^{3+}-doped fluoroaluminate glass by 0.655 μm excitation. *J Non-Cryst Solids.* 1991;135(1):90-93.

[16] Wang D, Guo Y, Sun G, Li J, Zhao L, Xu G. Blue, green, yellow and red upconversion

fluorescence in Tm^{3+}/Ho^{3+}:$Cs_2NaGdCl_6$ crystals under 785nm laser excitation. *J Alloys Compd.* 2008;451(1):122-124.

[17] Xu X, Zhao Z, Song P, Jiang B, Zhou G, Xu J, Deng P, Bourdet G, Chanteloup JC, Zhou J, Fulop A. Upconversion luminescence in Yb^{3+}-doped yttrium aluminum garnets. *Phys B.* 2005;357(3): 365-369.

[18] Malinowski M, Kaczkan M, Piramidowicz R, Frukacz Z, Sarnecki J. Cooperative emission in Yb3+: YAG planar epitaxial waveguides. *J Lumin*. 2001;94:29-33.

[19] Wang L, Li Y. $Na(Y_{1.5}Na_{0.5})F_6$ single-crystal nanorods as multicolor luminescent materials. *Nano Lett.* 2006;6(8): 1645-1649.

[20] Lin H, Meredith G, Jiang S, Peng X, Luo T, Peyghambarian N, Pun EYB. Optical transitions and visible upconversion in Er^{3+} doped niobic tellurite glass. *J Appl Phys.* 2002;93(1):186-191.

[21] Patra A, Friend CS, Kapoor R, Prasad PN. Effect of crystal nature on upconversion luminescence in Er^{3+}:ZrO_2 nanocrystals. *Appl Phys Lett.* 2003;83(2):284-286.

[22] Muhr V, Würth C, Kraft M, Buchner M, Baeumner AJ, Resch-Genger U, Hirsch T. Particle- size-dependent förster resonance energy transfer from upconversion nanoparticles to organic dyes. *Anal Chem.* 2017;89(9):4868-4874.

[23] Qiu J, Jiao Q, Zhou D, Yang Z. Recent progress on upconversion luminescence enhancement in rare-earth doped transparent glass-ceramics. *J Rare Earths.* 2016;34(4):341-367.

[24] Gouveia-Neto AS, da Costa EB, Bueno LA, Ribeiro SJL. Upconversion luminescence in transparent glass ceramics containing β-PbF_2 nanocrystals doped with erbium. *J Alloys*

Compd. 2004;375(1):224-228.

[25] Fedorov PP, Luginina AA, Popov AI. Transparent oxyfluoride glass ceramics. *J Fluorine Chem.* 2015;172:22-50.

[26] Wang X, Chu Y, Yang Z, Tian K, Li W, Wang S, Jia S, Farrell G, Brambilla G, Wang P. Broadband multicolor upconversion from Yb^{3+}-Mn^{2+} codoped fluorosilicate glasses and transparent glass ceramics. *Opt Lett.* 2018;43(20):5013-5016.

[27] Lin C, Bocker C, Rüssel C. Nanocrystallization in Oxyfluoride Glasses Controlled by Amorphous Phase Separation. *Nano Lett.* 2015;15(10):6764-6769.

[28] Pollnau M, Gamelin DR, Lüthi SR, Güdel HU, Hehlen MP. Power dependence of upconversion luminescence in lanthanide and transition-metal-ion systems. *Phys Rev B.* 2000;61(5):3337-3346.

[29] Song E, Chen Z, Wu M, Ding S, Ye S, Zhou S, Zhang Q. Room-temperature wavelength-tunable single-band upconversion luminescence from Yb^{3+}/Mn^{2+} codoped fluoride perovskites ABF_3. *Adv Opt Mater.* 2016;4(5):798-806.

Figure captions:

Fig. 1 (a) Si, (b) K, (c) Zn and (d) F atomic distributions resulting from MD simulations.

Fig. 2 Absorption spectra of doped glass and glass-ceramics and undoped glass samples.

Fig. 3 Photographs of 0.3 Yb^{3+}glass and GC samples: (a) glass under 980 nm laser pumping, (b) glass and GC illuminated by natural light.

Fig. 4 (a) Emission spectra of the Yb^{3+} doped fluorosilicate glass samples with different Yb^{3+} concentrations under 980 nm excitation. (b) Relation between max fluorescence intensity and Yb^{3+} concentration.

Fig. 5 Structural characterization of the 0.3Yb^{3+} -doped glass and GC heat-treated at 540 ˚C for 20 h. (a) XRD patterns and (b) HRTEM image of the corresponding nanocrystals in the GC.

Fig. 6 (a) Emission spectra of 0.3Yb^{3+} glass and GC samples obtained after 5, 10 and 20 h long thermal treatments. (b) Fluorescence lifetime of glass and GC samples obtained after 5 and 10 h long thermal treatments.

Fig. 7 (a) HAADF-STEM images of the 0.7 mol% Yb^{3+} doped GC samples, and corresponding STEM-EDS mappings for (b) Yb, (c) K, (d) F, (f) Si, (g) Zn, (h) O with their concentrations reflected by their brightness. (e) Schematic diagram of Yb^{3+} ions replacing Zn^{2+} ions in the $KZnF_3$ crystals.

Fig. 8 (a) Emission spectra of 0.3Yb^{3+} doped GC sample at different pump powers. The inset shows the relationship between fluorescence intensity (in logarithmic scale) and pump power, (b) energy level diagram of Yb^{3+} ions showing upconversion luminescence under excitation at 980 nm.