Broadband multicolor upconversion from Yb3+-Mn2+ codoped fluorosilicate glasses and transparent glass ceramics

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## In contrast to well-known upconversion (UC) emission from Yb3+-Mn2+ co-doped crystal, a room-temperature intense broadband UC phenomenon was first observed both in Yb3+-Mn2+ co-doped fluorosilicate glasses and transparent glass ceramics under 980 nm pumping. The obtained photoluminescence (PL) ranged from yellow to white to blue. We attributed this effect to the cooperative UC of Yb3+ and to the formation of Yb3+-Mn2+ pairs. After heat treatment, KZnF3 nanocrystals appeared in the glass matrix, as identified by X-ray diffraction (XRD) and transmission electron microscopy (TEM), and the emission intensity increased 45 times. We believe that Yb3+-Mn2+ co-doped glasses or glass ceramics show great potential as a material for multi-color displays.

**OCIS codes:** (140.3460) Lasers, (190.7110) upconversion; (300.6550) Spectroscopy, visible; (160.4670) Optical materials; (160.6990) Transition-metal-doped materials; (160.5690) Rare-earth-doped materials.

Upconversion (UC) refers to a nonlinear mechanism in which the sequential [absorption](https://en.wikipedia.org/wiki/Absorption_(electromagnetic_radiation)) of two or more photons leads to the emission of light at a shorter wavelength than the excitation wavelength [1-3]. Although this concept was first considered to be only a theoretical possibility [4], UC was later demonstrated in a number of materials, and shows potential for many applications such as biodetection [5], bioimaging [6], solar cells [7], 3D display technologies [8], and lasers [9, 10].

Most investigations of upconversion materials has focused on rare earth ions doped crystals [11-15], typically with Yb3+ as the sensitizer ion, which absorbs infrared radiation and non-radiatively transfers its excitation to activator ions such as Er3+, Tm3+ or Ho3+. Yet, the narrow emission band and the relatively unchanged emission wavelength limit their applications. Compared to rare earth ions, transition metal ions are closely associated with their surrounding chemical environment, resulting in a broadband emission and changeable emission peaks, desirable features for broadband tunable lasers.

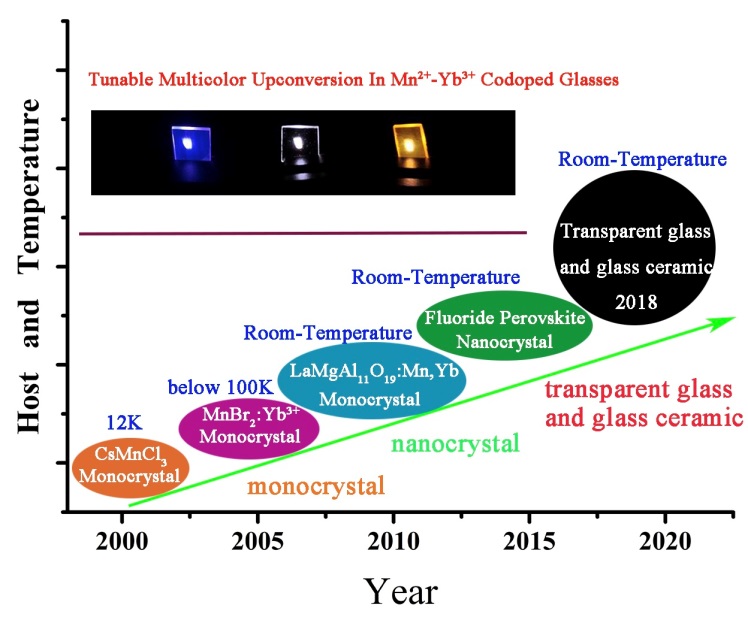


Fig. 1. Progress in upconversion of Mn2+ doped materials, digital photo: obtained glasses doped with different concentration of Yb3+.

Mn2+ is one of the transition metal ions that plays an important role in inorganic phosphors. The first example of upconversion between transition metal and rare earth ions was reported by R. Valiente et al. in 2000 [16]. Recently, Mn2+ doped and Yb3+-Mn2+ codoped materials have received increased attention because of the broadband tunable emission associated to the forbidden d-d transition 4T1(4G)→6A1(6S) [17,18]. Fig. 1 shows the progress of UC from Mn2+ doped materials, highlighting some breakthrough contributions. In 2001, R Valiente et al. firstly demonstrated Mn2+ UC in CsMnCl3 and RbMnCl3 monocrystal at the temperature T~12K [19]. In 2009, Martin-Rodriguez et al. broke through the temperature limit, obtaining broadband UC in LaMgAl11O19: Mn2+, Yb3+ monocrystal [20] at room-temperature. In 2016 Enhai Song et al. showed that single crystal is not necessary, by using a Yb3+-Mn2+ codoped fluoride perovskites ABF3 nanocrystals [21]. As distinct from the traditional Yb3+ sensitizer, Yb3+-Mn2+ pairs absorb 980 nm pump energy and obtain visible (VIS) broadband emission at room-temperature by achieving energy transfer (ET) directly from the energy level 2F5/2 [22]. Compared to crystal materials, glasses or glass ceramics have better light transmission, easier processing and thus lower preparation costs. Yet, there is little reported in the literature about Mn2+-Yb3+ co-doped glasses or transparent glass ceramics.

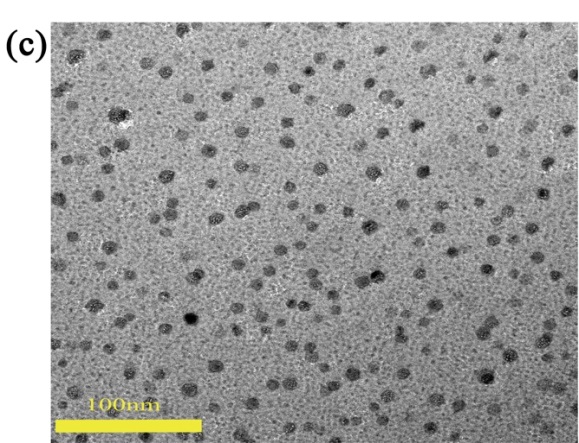
In this letter, we prepared both glasses and transparent glass ceramics containing Yb3+-Mn2+ codoped KZnF3 nanocrystals. Under λ~980 nm laser excitation, intense broadband UC emission from Mn2+ and Yb3+ was observed at room-temperature. When the Yb3+ content was changed, a multi-color emission from blue to white to yellow was observed, as shown in the inset of Fig. 1.

Glass samples of 22.5KF-(54.7-x)SiO2-22.5ZnF2-xYbF3-0.3MnO (x= 0, 0.1, 0.3, 0.6, 0.8 in mol%) were prepared by a conventional melt-quenching method. 40 g of pure KF (99.9%), SiO2 (99.9%), ZnF2 (99.9%), YbF3 (99.99%) and MnO (99.99%) powders were mixed in an agate mortar for at least 15 mins, stored in a platinum crucible and then put in an electric furnace at 1500 oC for 30 mins. The melt was cast onto a brass plate and pressed into a flake, annealed at 420 oC for 3 h to eliminate the inset press and to obtain the precursor glass (PG). The PGs were heated at 540 oC for 5 h, 10 h, 20 h to obtain the glass ceramics (GC) containing KZnF3 nanocrystals [23, 24]. To confirm the crystallization phase, X-ray diffraction (XRD) patterns were recorded by a D8 advance X-ray diffractometer (Bruker, Faellanden, Switzerland) with Cu-Kα irradiation. Nanocrystals morphology and size distribution were measured by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) (Tecnai G2, FEI, USA). The transmission and PL spectra of the obtained samples were recorded with a UV/VIS/NIR spectrophotometer (Lambda-900, PerkinElmer, USA) and a fluorescence spectrometer (FLS920, Edinburgh Instruments, UK), respectively.

Fig. 2 (a) shows the XRD patterns of the 0.3 Yb3+-0.3 Mn2+ codoped PG and GC samples with different heating treatment times. The broadband peak is attributed to the amorphous phase in the samples. The sharp peaks in the XRD patterns are distinguishable and both show features which match perfectly with the Joint Committee on Powder Diffraction Standards (JCPDS) Card of KZnF3 (No: 06-0439) crystal phase. The main crystal peaks at 2θ = 20.901o, 31.167o, 44.657o, 50.271o, 64.998o, 73.84o correspond to the crystal planes (100), (110), (200), (210), (220), (310), respectively. With increased heating treatment time, the diffraction peaks were more distinguishable. Fig. 2 (b) demonstrates the transmission spectra of 0.3Yb3+-0.3Mn2+ codoped PG and GC treated at T~540 oC for 20 h. The digital photo in the inset shows that the GC sample gets a little darker after thermal treatment, resulting in a transmittance attenuation of about 10% in the VIS wavelength region due







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Fig. 2. (a) XRD patterns of 0.3Yb3+-0.3Mn2+ PG sample, 0.3Yb3+-0.3Mn2+ GC samples of different heating treatment and KZnF3; (b) Transmission spectra of the PG and the GC (treated at T~540 oC for -20 h) GC samples, inset: digital photo of PG and GC samples with 2 mm thickness; (c) TEM image of the GC sample; (d) HRTEM image of the same GC sample.

to scattering. Fig. 2 (c) and (d) show the TEM and HTEM patterns of the same GC samples. KZnF3 nanocrystals are distributed uniformly in the glass phase and their sizes are in the range of 5 ~ 20 nm. This ultra-fine particle size allows these materials to be polished as they are in the glass state and then crystallized without any significant degradation of the surface quality. Fig. 2 (d) shows a series of lattice fringes of the KZnF3 crystal. The d-spacing of these crystal facets was measured to be 0.407 nm, which correspond to the crystal plane (100) of KZnF3.

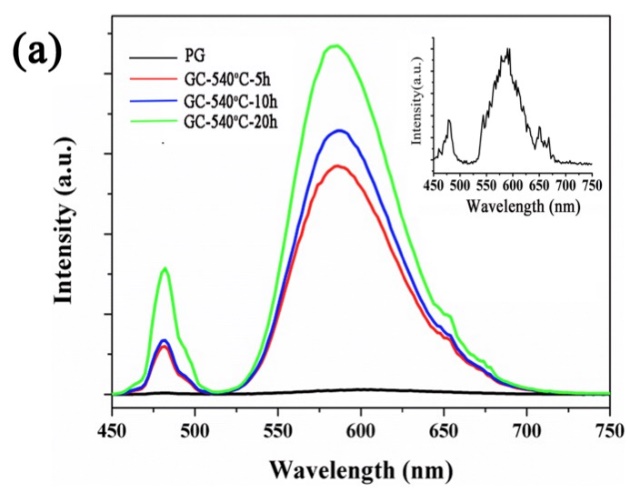




Fig. 3. (a) PL spectra of 0.3Yb3+-0.3Mn2+ doped PG and GC in the VIS wavelength region excited by 980 nm light, the inset is the PL spectrum of PG sample; (b) Schematic energy level diagram of the UC process.

Fig. 3 (a) shows the PL spectra of the 0.3Yb3+-0.3Mn2+ codoped PG and GC samples under the excitation of 980 nm LD. The emissions at 'λ~480 nm and 'λ~585 nm are attributed to the typical Yb3+-Yb3+ cooperative UC luminescence [25] and to the Yb3+-Mn2+ pairs UC processes [21] shown in Fig. 3 (b). The emission at 'λ~585 nm was observed in the PG sample, shown in the inset of Fig. 3 (a), which has not been reported previously. The intense emission was attributed to the structure of our samples. Phase separation in fluorosilicate glasses has already been confirmed by molecular dynamics (MD) simulations [26] and experiments [23]. In the fluoride-rich region, phonon energy and distance of ions are smaller than in the oxygen-rich region, thus it is possible to achieve ET between Yb3+-Mn2+ pairs. However, relatively high non-radiative probability still exists in the oxygen-rich region, as it is also in the glass form, resulting in weak luminescence. In the GC samples, KZnF3 nanocrystals provide a strong crystal field environment for both Mn2+ and Yb3+, thus the non-radiative probability is much lower compared to the PG, producing the enhanced emission. The intensity of the Mn2+ broadband emission of GC is 45 times higher than that of the PG. With increasing the treatment time, the size of KZnF3 becomes bigger and the crystal field becomes stronger, resulting in the enhanced emission. The mechanism of broadband emission was shown in Fig. 3 (b). When the distance between Yb3+ and Mn2+ was small enough, the Yb3+-Mn2+ pair is formed, leading to the establishment of a series of new energy levels. The energy levels |2F7/2, 6A1(6S)> , |2F5/2, 6A1(6S)> , |2F7/2, 4T1(4G)> were the ground state, intermediate hybrid excited state and emitting state, respectively. Under the excitation of the λ~980 nm laser, the ground state absorption (GSA) produced excitation of the Yb3+-Mn2+ pairs into the |2F5/2, 6A1(6S)> state. Meanwhile, the excited state absorption (ESA) occurred, populating the emitting state |2F5/2, 6A1(6S)>, which then emits a photon in the visible.



Fig. 4. (a) emission spectra of 0.3Yb3+-0.3Mn2+ codoped PG samples upon different pump power; (b) double-logarithmic plots of the pump-power dependent on UC emission of Mn2+ and Yb3+; (c) emission spectra of 0.3Mn2+-xYb3+ (x=0.1, 0.3, 0.6, 0.8) codoped PG samples(d) CIE chromaticity coordinates of different content of Yb3+. All excitation:980 nm LD.

To obtain more detailed information about the UC emission of Mn2+, the pump power-dependent UC emissions were investigated, as shown in Fig. 4 (a). The luminescence intensities both increase with increasing pump powers. The relationship between the UC intensity (*IUC*) and the pumped power (*Ipump*) can be fitted as: *Iuc* ∞ (*Ipump*)n, where *n* represents the absorbed photon numbers per VIS or near-infrared (NIR) photon emitted, and the values can be obtained from the slope of the fitted line of the plot of log *IUC* versus log (*Ipump*)*n,* as shown in Fig. 4 (b) [27, 28]. Therefore, the higher is the pump power density of the laser, the higher is the emission intensity achieved. The linear fits slopes of log (*IUC*) - log (*Ppump*) for the λ~480 nm and λ~580 nm are 1.6173 and 1.6419, respectively, involving a two-photon process in the UC emission. Fig. 4 (c) shows the normalized PL spectra of xYb3+-0.3Mn2+ codoped PG samples (x=0.1, 0.3, 0.6, 0.8). Fig. 4 (d) gives the CIE chromaticity coordinates based on their UC emission spectra, shown in Fig. 4 (c). The UC emission color can be tuned from blue to white to yellow with decreasing the content of Yb3+.

In summary, a series of Yb3+-Mn2+ codoped glasses and transparent glass ceramics containing KZnF3 nanocrystals were fabricated. Under 980 nm LD pumping, two room-temperature UC emission centered at around λ~480 nm and λ~585 nm were observed, with the emission intensities increasing when the KZnF3 nanocrystals appeared in glass matrix. These emissions can be interpreted by two photon UC mechanism based on the coupled Yb3+-Yb3+ and Yb3+-Mn2+ pairs. The relative intensity of the two emission peaks can be adjusted by changing the concentration of Yb3+ ions to achieve a tunable multicolor emission. This kind of material shows promise for applications in various fields, such as tunable lasers, lighting, displays, imaging, and biosensors.

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**REFERENCES**

1. F. Auzel, Cheminform **104**, 139 (2004).

2. M. Haase and H. Schäfer, Angew. Chem. Int. Ed. **50**, 5808 (2011).

3. B. Zhou, B. Shi, D. Jin, and X. Liu, Nat. Nanotechnol. **10**, 924 (2015).

4. N. Bloembergen, Phys. Rev. Lett. **2**, 84 (1959).

5. Z. C, Y. Y, Z. S, W. Y, and L. Z, Angew. Chem. Int. Ed. **50**, 6851 (2011).

6. M. Nyk, R. Kumar, T. Y. Ohulchanskyy, E. J. Bergey, and P. N. Prasad, Nano Lett. **8**, 3834 (2008).

7. W. Zou, C. Visser, J. A. Maduro, M. S. Pshenichnikov, and J. C. Hummelen, Nat. Photonics **6**, 560 (2012).

8. F. Wang, Y. Han, C. S. Lim, Y. Lu, J. Wang, J. Xu, H. Chen, C. Zhang, M. Hong, and X. Liu,nature **463**, 1061 (2010).

9. Z. Luo, Q. Ruan, M. Zhong, Y. Cheng, R. Yang, B. Xu, H. Xu, and Z. Cai, Opt. Lett. **41**, 2258 (2016).

10. Y. Ma, Y. Li, J. Feng, and K. Zhang, Opt. Express **26**, 12106 (2018).

11. Y. Liu, Q. Yang, G. Ren, C. Xu, and Y. Zhang, J. Alloys Compd. **467**, 351 (2009).

12. J. Jin, Y.-J. Gu, C. W.-Y. Man, J. Cheng, Z. Xu, Y. Zhang, H. Wang, V. H.-Y. Lee, S. H. Cheng, and W.-T. Wong, ACS Nano **5**, 7838 (2011).

13. W. Yin, L. Zhao, L. Zhou, Z. Gu, X. Liu, G. Tian, S. Jin, L. Yan, W. Ren, and G. Xing, Chem. Eur. J. Journal **18**, 9239 (2012).

14. J. Sun, J. Xian, and H. Du, J. Phys. Chem. Solids **72**, 207 (2011).

15. G. Chen, T. Y. Ohulchanskyy, R. Kumar, H. Ågren, and P. N. Prasad,ACS Nano **4**, 3163 (2010).

16. R. Valiente, O. Wenger, and H. U. Güdel, Chem. Phys. Lets. **320**, 639-644 (2000).

17. P. Gerner, O. S. Wenger, R. Valiente, and H. U. Güdel, Inorg. Chem. 40, 4534 (2001).

18. R. Martín-Rodríguez, R. Valiente, F. Rodríguez, F. Piccinelli, A. Speghini, and M. Bettinelli, Phys. Rev. B 82, 075117 (2010)

19. C. Reinhard, P. Gerner, R. Valiente, O. Wenger, and H. U. Güdel, J. Lumin. **94**, 331 (2001).

20. R. Martín-Rodríguez, R. Valiente, and M. Bettinelli, Appl. Phys. Lett. **95**, 091913 (2009).

21. E. Song, Z. Chen, M. Wu, S. Ding, S. Ye, S. Zhou, and Q. Zhang, Adv. Opt. Mater. **4**, 798 (2016).

22. Y. Chu, J. Ren, J. Zhang, G. Peng, J. Yang, P. Wang, and L. Yuan, Sci. Rep. **6**, 33865 (2016).

23. C. Lin, C. Bocker, and C. Rüssel, Nano Lett. **15**, 6764 (2015).

24. C. Lin, L. Li, S. Dai, C. Liu, Z. Zhao, C. Bocker, and C. Rüssel, J. Phys. Chem. C **120**, 4556 (2016).

25. P. Goldner, B. Schaudel, and M. Prassas,. Phys. Rev. B 65, 054103 (2002).

26. J. Zhao, R. Ma, X. Chen, B. Kang, X. Qiao, J. Du, X. Fan, U. Ross, C. Roiland, and A. Lotnyk, J. Phys. Chem. C **120**, 17726-17732 (2016).

27. M. Pollnau, D. R. Gamelin, S. Lüthi, H. Güdel, and M. Hehlen, Phys. Rev. B **61**,3337 (2000).

28. X. Wu, J. Denis, G. Özen, P. Goldner, and F. Pellé, Appl. Phys. B: Photophys. Laser Chem. **56**, 269-273 (1993).

**Full citation listings**

1. F. Auzel, "Upconversion and anti-Stokes processes with f and d ions in solids," Cheminform **104**, 139 (2004).

2. M. Haase and H. Schäfer, "Upconverting nanoparticles," Angewandte Chemie International Edition **50**, 5808-5829 (2011).

3. B. Zhou, B. Shi, D. Jin, and X. Liu, "Controlling upconversion nanocrystals for emerging applications," Nature Nanotechnology **10**, 924 (2015).

4. N. Bloembergen, "Solid State Infrared Quantum Counters," Physical Review Letters **2**, 84-85 (1959).

5. Z. C, Y. Y, Z. S, W. Y, and L. Z, "Biosensing platform based on fluorescence resonance energy transfer from upconverting nanocrystals to graphene oxide," Angewandte Chemie International Edition **50**, 6851-6854 (2011).

6. M. Nyk, R. Kumar, T. Y. Ohulchanskyy, E. J. Bergey, and P. N. Prasad, "High contrast in vitro and in vivo photoluminescence bioimaging using near infrared to near infrared up-conversion in Tm3+ and Yb3+ doped fluoride nanophosphors," Nano Letters **8**, 3834 (2008).

7. W. Zou, C. Visser, J. A. Maduro, M. S. Pshenichnikov, and J. C. Hummelen, "Broadband dye-sensitized upconversion of near-infrared light," Nature Photonics **6**, 560-564 (2012).

8. F. Wang, Y. Han, C. S. Lim, Y. Lu, J. Wang, J. Xu, H. Chen, C. Zhang, M. Hong, and X. Liu, "Simultaneous phase and size control of upconversion nanocrystals through lanthanide doping," nature **463**, 1061 (2010).

9. Z. Luo, Q. Ruan, M. Zhong, Y. Cheng, R. Yang, B. Xu, H. Xu, and Z. Cai, "Compact self-Q-switched green upconversion Er: ZBLAN all-fiber laser operating at 543.4 nm," Optics letters **41**, 2258-2261 (2016).

10. Y. Ma, Y. Li, J. Feng, and K. Zhang, "Influence of energy-transfer upconversion and excited-state absorption on a high power Nd: YVO 4 laser at 1.34 μm," Optics express **26**, 12106-12120 (2018).

11. Y. Liu, Q. Yang, G. Ren, C. Xu, and Y. Zhang, "Relationship between microstructure and the achieving of the single-band red upconversion fluorescence of Er3+/Yb3+ codoped crystallites," Journal of Alloys and Compounds **467**, 351-356 (2009).

12. J. Jin, Y.-J. Gu, C. W.-Y. Man, J. Cheng, Z. Xu, Y. Zhang, H. Wang, V. H.-Y. Lee, S. H. Cheng, and W.-T. Wong, "Polymer-coated NaYF4: Yb3+, Er3+ upconversion nanoparticles for charge-dependent cellular imaging," ACS nano **5**, 7838-7847 (2011).

13. W. Yin, L. Zhao, L. Zhou, Z. Gu, X. Liu, G. Tian, S. Jin, L. Yan, W. Ren, and G. Xing, "Enhanced red emission from GdF3: Yb3+, Er3+ upconversion nanocrystals by Li+ doping and their application for bioimaging," Chemistry-A European Journal **18**, 9239-9245 (2012).

14. J. Sun, J. Xian, and H. Du, "Hydrothermal synthesis of BaYF5: Yb3+/Er3+ upconversion luminescence submicrospheres by a surfactant-free aqueous solution route," Journal of Physics and Chemistry of Solids **72**, 207-213 (2011).

15. G. Chen, T. Y. Ohulchanskyy, R. Kumar, H. Ågren, and P. N. Prasad, "Ultrasmall monodisperse NaYF4: Yb3+/Tm3+ nanocrystals with enhanced near-infrared to near-infrared upconversion photoluminescence," ACS nano **4**, 3163-3168 (2010).

16. R. Valiente, O. Wenger, and H. U. Güdel, "New photon upconversion processes in Yb3+ doped CsMnCl3 and RbMnCl3," Chemical Physics Letters **320**, 639-644 (2000).

17. P. Gerner, O. S. Wenger, R. Valiente, and H. U. Güdel, "Green and red light emission by upconversion from the near-IR in Yb3+ doped CsMnBr3," Inorganic chemistry **40**, 4534-4542 (2001).

18. R. Martín-Rodríguez, R. Valiente, F. Rodríguez, F. Piccinelli, A. Speghini, and M. Bettinelli, "Temperature dependence and temporal dynamics of Mn2+ upconversion luminescence sensitized by Yb3+ in codoped LaMgAl11O19," Physical Review B **82**, 075117 (2010).

19. C. Reinhard, P. Gerner, R. Valiente, O. Wenger, and H. U. Güdel, "Upconversion phenomena in the Yb3+ doped transition metal compounds Rb2MnCl4 and CsMnBr3," Journal of luminescence **94**, 331-335 (2001).

20. R. Martín-Rodríguez, R. Valiente, and M. Bettinelli, "Room-temperature green upconversion luminescence in LaMgAl11O19: Mn2+, Yb3+ upon infrared excitation," Applied Physics Letters **95**, 091913 (2009).

21. E. Song, Z. Chen, M. Wu, S. Ding, S. Ye, S. Zhou, and Q. Zhang, "Room‐Temperature Wavelength‐Tunable Single‐Band Upconversion Luminescence from Yb3+/Mn2+ Codoped Fluoride Perovskites ABF3," Advanced Optical Materials **4**, 798-806 (2016).

22. Y. Chu, J. Ren, J. Zhang, G. Peng, J. Yang, P. Wang, and L. Yuan, "Ce3+/Yb3+/Er3+ triply doped bismuth borosilicate glass: a potential fiber material for broadband near-infrared fiber amplifiers," Scientific reports **6**, 33865 (2016).

23. C. Lin, C. Bocker, and C. Rüssel, "Nanocrystallization in oxyfluoride glasses controlled by amorphous phase separation," Nano letters **15**, 6764-6769 (2015).

24. C. Lin, L. Li, S. Dai, C. Liu, Z. Zhao, C. Bocker, and C. Rüssel, "Oxyfluoride glass-ceramics for transition metal ion based photonics: broadband Near-IR luminescence of nickel ion dopant and nanocrystallization mechanism," The Journal of Physical Chemistry C **120**, 4556-4563 (2016).

25. P. Goldner, B. Schaudel, and M. Prassas, "Dependence of cooperative luminescence intensity on Yb3+ spatial distribution in crystals and glasses," Physical Review B **65**, 054103 (2002).

26. J. Zhao, R. Ma, X. Chen, B. Kang, X. Qiao, J. Du, X. Fan, U. Ross, C. Roiland, and A. Lotnyk, "From phase separation to nanocrystallization in fluorosilicate glasses: structural design of highly luminescent glass-ceramics," The Journal of Physical Chemistry C **120**, 17726-17732 (2016).

27. M. Pollnau, D. R. Gamelin, S. Lüthi, H. Güdel, and M. Hehlen, "Power dependence of upconversion luminescence in lanthanide and transition-metal-ion systems," Physical Review B **61**, 3337 (2000).

28. X. Wu, J. Denis, G. Özen, P. Goldner, and F. Pellé, "The UV, blue and green up-conversion luminescence of PbF 2+ GeO 2: Er 2 O 3 pumped with 650 nm," Applied Physics B **56**, 269-273 (1993).