Anti-escaping of incident laser in rare-earth doped fluoride ceramics with glass forming layer

H. F. Shi, P. J. Lin, J. X. Yang, J. L. Yuan, E. Y. B. Pun, Y. Song, X. Zhao* & H. Lin

Adaptive fluoride ceramic with glass forming layer (GC\textsubscript{ZBL}-Er) used in laser anti-escaping has been prepared by one-step synthesis, and the thickness of glass layer is identified as ~0.41 mm. Blue, green and red emissions of Er\textsuperscript{3+}/Yb\textsuperscript{3+} codoped fluoride ceramic (C\textsubscript{ZBL}-Er) and glass layer (G\textsubscript{ZBL}-Er) have been investigated under ~980 nm laser pumping. With the forming of thin glass layer on ceramic surface, the absorption intensities on diffuse reflection of GC\textsubscript{ZBL}-Er at 974 nm and 1.53 \textmu m increase by 48% and 53% than those of C\textsubscript{ZBL}-Er. Excited by a 979 nm laser, the presence of the glass layer increases the absolute absorption rate in spectral power from 75% in C\textsubscript{ZBL}-Er to 83% in GC\textsubscript{ZBL}-Er, which is consistent with the improvement in the absorbed photon number. In addition, the quantum yield of GC\textsubscript{ZBL}-Er complex is raised by 28.4% compared to the case of ceramic substrate by photon quantification. Intense absorption-conversion ability and efficient macroscopical anti-escaping effect confirm the superiority of ingenious structure in the fluoride ceramics with glass forming layer, which provides a new approach for developing the absorption-conversion materials of anti-NIR laser detection.

With the development of modern optical technology, the laser device has been widely employed in material processing, laser designator, medical diagnosis and other fields\textsuperscript{1–3}. Nowadays, the laser beams applied in optical communication and laser ranging include the 1.54 \textmu m erbium (Er\textsuperscript{3+}) doped glass laser and 980 nm high-power semiconductor laser\textsuperscript{4–17}. Detection laser devices operate by two principles, one of which is to irradiate the laser beam on the attack target directly, such as laser blinding equipment, and then the other is to emit laser to the target and further receive the reflected wave, including ranging and semi-active laser guidance\textsuperscript{18–22}. As the generation of laser equipment makes laser a threat for human heathy, the development of laser protection receives sustained attention. Absorptive typed laser-protective materials have been accredited as excellent candidates due to their wide applicability and convenient preparation\textsuperscript{23–27}. On this basis, it is necessary to take some measures to greatly attenuate the intensity of the laser beam to achieve laser anti-escaping, which makes it better for anti-NIR laser detecting.

Rare earth (RE) elements possess unfilled 4f electron layer structure, which produces a variety of energy levels, determining that RE ions doped materials can absorb photons of different wavelengths\textsuperscript{28–41}. Among multitudinous RE ions, the level structure of Er\textsuperscript{3+} is rich and uniform, and Er\textsuperscript{3+} has strong absorption capacity in the ~980 nm and ~1.53 \textmu m ranges commonly used in laser detection\textsuperscript{42–50}. In addition, Yb\textsuperscript{3+} ion as sensitized ion can further absorb the NIR radiation efficiently and transfer the excitation energy to Er\textsuperscript{3+} via energy transfer processes, which can achieve large NIR laser absorption and efficient up-conversion emission, presenting a great potential in laser protection materials\textsuperscript{51–59}. At present, the glass matrix typed laser protective material can overcome the shortcomings of the poor heat resistance, easy aging and low chemical resistance of the plastic matrix typed. However, the absorption ability of the general glass matrix typed material to laser is difficult to meet the application of the anti-NIR laser detection. Therefore, the exploration focusing on a new-type compound material with excellent absorption-conversion ability and high heat resistance potential becomes urgent in the future.

In this work, enhanced typed fluoride ceramic with glass forming layer has been prepared by one-step synthesis, and the laser stealth and interference can be realized based on the principle of RE\textsuperscript{3+} absorption, light conversion and energy transfer for NIR detecting laser. The complex reflection process between the glass-ceramic transition region and glass layer promotes the continuous consumption of incident laser, which obviously...
improves the absorption efficiency of the GZBL-Er. Here, the statement "anti-escape" is used to describe the material good absorption effect for incident laser light. In particular, the laser signals detected and tracked at 980 nm and 1.53 μm are strongly absorbed and converted into other wavelength light radiations. These results confirm that the special structure of fluoride ceramic equipped with glass layer can enhance absorption-conversion efficiency and laser anti-escaping effect for incident NIR rader laser.

**Discussion**

**Structure and morphology property.** To reveal absorption-conversion efficiency for NIR detecting laser, 1.0 wt% ErF₃ and 2.0 wt% YbF₃ as dopants are introduced into fluorozirconate matrix and denoted as GCZBL-Er, and individual glass and ceramic phase are labeled as GZBL-Er and CZBL-Er, respectively. XRD pattern of as-synthesized GZBL-Er powder exhibits a broad diffuse scattering at lower angles rather than the narrow diffraction peaks for crystal phase, and the amorphous nature of the GZBL-Er glass layer is well identified, as exhibited in Fig. 1(a). In addition, the detected diffraction peaks of CZBL-Er are in accordance well with the standard BaZrF₆ (JCPDS 76–1699), and the derived cell parameters (a = 7.744 Å, b = 11.691 Å, c = 5.404 Å, α = β = γ = 90°) of CZBL-Er are coincide with those of BaZrF₆ phase (a = 7.681 Å, b = 11.357 Å, c = 5.511 Å, α = β = γ = 90°), indicating the formation of the pure BaZrF₆ phase in upper layer of GCZBL-Er composite. Meanwhile, a little difference in cell parameters is attributed to the crystalline environment variation and the lattice deformation with the introduction of Er³⁺ and Yb³⁺ ions to some extent.

The microstructure and morphology of as-synthesized GCZBL-Er composite is explored, and the SEM image of the glass-ceramic transition region is displayed in Fig. 1(b). The interface between the glass and ceramic phase is obvious and uniform, and the thickness of the glass layer is measured to be ~0.41 mm under the optical microscope. In addition, the grain size of the ceramics phase in Fig. 1(c,d) is identified to be 550 × 120 nm, and the crystalline phase of the rectangular structure with neat arrangement is further judged as the aggregation of several BaZrF₆ crystallites.

Under 980 nm laser excitation, the emission spectra of GZBL-Er and CZBL-Er powders with sundry pumping powers are depicted in Fig. 2(a,b), and four emission bands centered at 408, 522, 544 and 653 nm are attributed to f-f transitions ⁴S₃/₂ → ⁴I₁₅/₂, ⁴H₁₁/₂ → ⁴I₁₅/₂, ⁴I₉/₂ → ⁴I₁₅/₂ and ⁴F₉/₂ → ⁴I₁₅/₂, respectively. As the excitation power increases, the intensity of each peak increases exponentially, and the upconversion emission intensity Iₙlumin is proportional to the nth power of the 980 nm excitation intensity Iₙexcit, which can be simply expressed as Iₙlumin ∝ Iₙexcitⁿ, where Iₙlumin is fluorescence intensity, Iₙexcit is excitation power and n is the number of 980 nm photons absorbed per visible photon emitted. In addition, the intense upconversion green and red emissions are

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**Figure 1.** (a) XRD patterns of GZBL-Er and CZBL-Er powders. SEM images of (b) the glass-ceramic transition region and (c,d) the ceramic region of GCZBL-Er. Inset: Corresponding photographys under fluorescence microscope.
confirmed to be two-photon absorption processes as indicated in Fig. 2(c,d), besides, rare 408 nm blue emission is identified as three-photon absorption process in the low phonon energy material.

In fluorozirconate glass system, the polyhedral network structure is formed mainly through Zr−F−Zr bridging, promoting the GZBL-Er sample with low phonon energy $\sim 570$ cm$^{-1}$. The characteristic can reduce the probability of non-radiative transition, which reflects intuitively in 544 nm emission of Er$^{3+}$. The fluorescence decay curves of the 4S3/2 level for GZBL-Er and CZBL-Er layer monitored at 544 nm are exhibited in the inset of Fig. 2(a,b). In addition, the fluorescent lifetimes ($\tau_{\text{exp-avg}}$) of GZBL-Er and CZBL-Er are up to be 461.9 and 558.5 $\mu$s, respectively, which far exceed to 58 $\mu$s in Li$_2$B$_4$O$_7$ glass$^{62}$, 26 $\mu$s in SrF$_2$ nanocrystals$^{63}$, 333 $\mu$s in NaYF$_4$ $^{64}$ and are close to 490 $\mu$s in oxyfluoride tellurite$^{65}$, indicating that the low phonon-energy material contributes to photon releasing effectively.

Enhanced absorption effect and principle analysis of GCZBL-Er. Although the optical transition capability of the glass fluorescent material to NIR laser are not as intense as crystal materials, when a glass forming layer is compounded on fluoride ceramics, the situation will be reversed. As exhibited in Fig. 3(a), the absorption intensities of GCZBL-Er at 974 and 1532 nm are $\sim 1.48$ and $\sim 1.53$ times higher than those in CZBL-Er, meanwhile. Correspondingly, the derived reflectance curve shown in Fig. 3(b) more clearly indicates that the reflectivity is reduced from 50% to 36% with the existence of thin glass layer. The reflected laser intensity including the Fresnel reflection is uniformly distributed and fully recorded in the integrating sphere, and the intensity ratio of the reflected laser to incident laser can analyze the reflection ability of the material more macroscopically. Besides, the molar absorption coefficient $\alpha_{\text{OH}}$ can be used to evaluate the residual OH content in glass samples and is derived to be 0.91 cm$^{-1}$ in 75TeO$_2$–10ZnO–10Na$_2$O–5GeO$_2$ glasses$^{66}$, while the value in this work glass is as low as 0.57 cm$^{-1}$. The FT-IR spectrum of glass layer is shown in Fig. 3(c), and the low OH content is beneficial for anticipated photon emitting of this material. The apparent improvement can be attributed to the complex surface morphology of ceramic matrix and the intense dispersion effect of glass layer, and the schematic diagram of the absorption mechanism is shown in Fig. 3(d). When the detection laser is incident into the composite material GCZBL-Er, it will be absorbed by the glass phase in the reflection process of the glass-ceramic transition region. Then the residual laser is re-reflected to the ceramic boundary owing to the specular effect of the glass layer, forming a multiple-cycle effect, which heightens the absorption ability effectively of GCZBL-Er for NIR laser. In addition, the interface of the glass to ceramic region in schematic diagram is a rough outline, while the actual
surface topography is more complicated in fact. So the absorption effect of NIR incident laser is greatly increased with the complexity of the reflection process in the GCZBL-Er composite material. Just as the inset of Fig. 3(d), the facula area of GCZBL-Er is bigger than CZBL-Er and the luminous intensity is brighter at the same condition, showing that the GCZBL-Er composite increases the absorption intensity effectively to the NIR incident laser with the forming of thin glass layer on ceramic surface. Besides, the surface of formed glass is quietly smooth and further can effectively solve the follow-up cleaning problems in application. These results indicate that the complex structure of GCZBL-Er can be employed to enhance the absorption efficiency of ∼980 nm and ∼1.53 μm wavelengths, further exhibiting a laser anti-escaping effect.

Photon quantification on absorption-conversion potential of CZBL-Er and GCZBL-Er. In order to quantitatively characterize on absorption-conversion behavior of CZBL-Er and GCZBL-Er for laser beam, integrating sphere coupled with a CCD detector is applied to measure the absolute spectral parameters, which provides external quantum yield (QY) to evaluate luminescence and laser materials. Figure 4 presents the spectral power distributions as a function of 979 nm laser pumping power in CZBL-Er and GCZBL-Er samples, and the measured excitation powers are selected as 33, 106, 264, 400, 549 and 701 mW, respectively. Here, to ensure the laser fully diverged in integrating sphere, each sample is placed obliquely at the same angle and keeps a distance from the laser head. Besides, the tilt angle of the sample, the divergence angle of the laser and the distance of the laser head to the sample are measured to derive the area of the laser spot. Based on the above, the laser excitation power densities of the sample are further determined to be 16, 52, 129, 196, 269 and 344 mW/mm², respectively. Taking the high-power 701 mW and low-power 106 mW incident laser as an example, the 980 nm incident laser, the residual lasers on the excited glass surface and ceramic surface are measured as shown in Fig. 5. Furthermore, the absorption ratio of CZBL-Er to the incident laser is as high as 75.1% and 75.0% under 979 nm laser with 701 mW and 106 mW powers, respectively. Surprisingly, when the glass layer of GCZBL-Er sample faces laser head, the absorption rates further rise to 83.4% and 82.9%, which is attributed to the intense dispersion of laser beam between glass and ceramic, proving that the special structure of composite glass layer is more suitable for the absorption of NIR laser light.

As a clear resolution of the photon number cumulative conversion effect, the photon number distribution can further elaborate the up-conversion emission law of the sample. The photon quantization is adopted to explain the enhanced absorption-conservation ability and anti-escaping effect of glass layer to NIR lasers. Based on the net spectral power distribution, the photon number distribution can be derived by $N(\nu) = \frac{h}{\lambda^3} P(\lambda)$, where $\lambda$ is the wavelength, $\nu$ is the wavenumber, $h$ is the Planck constant, $c$ is the vacuum light velocity, and $P(\lambda)$ is spectral power distribution. The net absorption and emission photon distribution curves of CZBL-Er and GCZBL-Er are derived as presented in Fig. 6, and the integrated values are listed in Table 1. The green, red and NIR emissions at 522, 543, 665 and 848 nm are assigned to the $^2H_{11/2} \rightarrow ^4I_{15/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$, $^2F_{5/2} \rightarrow ^4I_{15/2}$ and $^4S_{3/2} \rightarrow ^4I_{13/2}$ transitions.
of Er$^{3+}$, respectively. In addition, the intense UC 848 nm emission is not easy to obtain, which provides more sufficient approaches for the conservation of incident laser. Since the ceramic substrate composites the glass layer, the emission intensity of GCZBL-Er at wavenumber is stronger than that in CZBL-Er material. When laser power density is selected to be 129 mW/mm$^2$, the net emission photons of four emissions at 522, 543, 665 and 848 nm are as high as $2.31 \times 10^{14}$, $11.49 \times 10^{14}$, $10.38 \times 10^{14}$ and $6.62 \times 10^{14}$ cps of CZBL-Er, respectively. Moreover, with the formation of the glass layer, emission photons further improve and reach to be $3.56 \times 10^{14}$, $16.48 \times 10^{14}$, $13.24 \times 10^{14}$, $8.75 \times 10^{14}$ cps in GCZBL-Er, respectively. In addition, the enhanced percentage of total emitted photon number shows a trend of improving first and then decreasing slightly with the increase of laser pumping power. Figure 7(a,b) show the emission photon number of CZBL-Er and GCZBL-Er under the 979 nm laser with different excitation power density, where the rising tendency of the above four emission photons become dramatically severe, manifesting that the two-photon-excited luminescence has a positive dependency on the excitation power density.

The photoluminescence quantum yield (QY) is conducive to judge the luminous characters of optical materials, which provides a direct evaluation for the laser absorption-conversion efficiency. Thus the absolute fluorescence parameter of QY for CZBL-Er and GCZBL-Er are carried out based on $QY = \frac{N_{em}}{N_{abs}}$, where the $N_{abs}$ and $N_{em}$ represent the net absorption photon number and net emission photon number. The QYs for green, red and NIR UC emission of CZBL-Er and GCZBL-Er under 979 nm NIR laser with different pumping power densities are listed in Table 1 and illustrated in Fig. 7(c,d). As listed in Table 2, the total QYs of CZBL-Er and GCZBL-Er reach to be $0.86 \times 10^{-4}$-$11.74 \times 10^{-4}$ and $0.96 \times 10^{-4}$-$14.67 \times 10^{-4}$, respectively. The QY of the GCZBL-Er up to $7.96 \times 10^{-4}$ is solved under the excitation of 129 mW/mm$^2$ power density, which is 28.4% more than that of CZBL-Er. The QYs of green and red emissions from Er$^{3+}$ and Ho$^{3+}$ in different glass matrices are listed in Table 3. As can be seen from the data, the high quantum yield in GCZBL-Er sample is over ten times higher than the values of BALMT glass, NMAG glass, BZYTLE glass and other oxide glasses. However, the quantum yield in fluoride glass exceeds that of GCZBL-Er, which is attributed to the superior absorption capacity of the composite with
special structure. With the enhancing incident laser power densities, the number of photons emitted increases exponentially, and the quantum yield improves continuously, which indicates that both absorption and emission of CZBL-Er and GCZBL-Er for NIR laser are still not saturated. Taken together, these results manifests that the forming of glass layer on ceramic substrate not only improves the absorption for NIR laser by the multi-reflection process, but also greatly enhances the optical-conversion ability, which confirms the GCZBL-Er complex processes a potential applied in anti-escaping of incident laser.

Figure 6. Net emission photon distributions in (a–d) CZBL-Er and (e–h) GCZBL-Er under the 979 nm laser excitation. Insets: details of related net absorption photon distributions of CZBL-Er and GCZBL-Er under the excitation of 979 nm laser in an integrating sphere.
Conclusion

Multi-photon-excited blue, green, red and NIR emissions have been quantified in Er$^{3+}$/Yb$^{3+}$ doped fluoride ceramic (CZBL-Er) and glass layer (GZBL-Er). The fluorescent lifetimes of GZBL-Er and CZBL-Er are up to be 461.9 and 558.5 μs, which indicates the fluorozirconate system can achieve effective photon releasing due to low maximum phonon energy. The absorption intensity of GCZBL-Er at 974 and 1532 nm are determined to be $\sim$1.48 and $\sim$1.53 times higher than those in CZBL-Er, and the absorption enhancement is attributed to the reflection of complex surface morphology on ceramic substrates and the diffusion absorption of glass layers. With the forming of

| Excitation power density (mW/mm²) | Sample    | Net absorption photon number (10^16cps) | Enhanced percentage (%) | Emission photon number (10^14cps) | Enhanced percentage (%) |
|-----------------------------------|-----------|----------------------------------------|-------------------------|-----------------------------------|-------------------------|
|                                   | CZBL-Er   | 11.48                                  | 11.4                    | $^2H_{11/2} \rightarrow ^4I_{15/2}$ | 0.005                   |
|                                   | GZBL-Er   | 12.79                                  |                         | $^4S_{3/2} \rightarrow ^4I_{15/2}$ | 0.043                   |
| 16                                | CZBL-Er   | 38.96                                  | 10.2                    | $^4F_{9/2} \rightarrow ^4I_{13/2}$ | 0.023                   |
| 52                                | GZBL-Er   | 42.93                                  |                         | $^4S_{3/2} \rightarrow ^4I_{13/2}$ | 0.025                   |
| 129                               | CZBL-Er   | 97.05                                  | 9.9                     | $^2H_{11/2} \rightarrow ^4I_{15/2}$ | 1.89                    |
|                                   | GZBL-Er   | 106.67                                 |                         | $^4S_{3/2} \rightarrow ^4I_{15/2}$ | 1.33                    |
| 196                               | CZBL-Er   | 148.08                                 | 10.0                    | $^4F_{9/2} \rightarrow ^4I_{13/2}$ | 2.668                   |
|                                   | GZBL-Er   | 162.87                                 |                         | $^4S_{3/2} \rightarrow ^4I_{13/2}$ | 1.830                   |
| 269                               | CZBL-Er   | 205.03                                 | 8.6                     | $^2H_{11/2} \rightarrow ^4I_{15/2}$ | 6.356                   |
|                                   | GZBL-Er   | 222.76                                 |                         | $^4S_{3/2} \rightarrow ^4I_{15/2}$ | 4.423                   |
| 344                               | CZBL-Er   | 259.29                                 | 10.4                    | $^2H_{11/2} \rightarrow ^4I_{15/2}$ | 10.376                  |
|                                   | GZBL-Er   | 286.36                                 |                         | $^4S_{3/2} \rightarrow ^4I_{15/2}$ | 6.268                   |
| 384                               | CZBL-Er   | 384.86                                 |                         | $^2H_{11/2} \rightarrow ^4I_{15/2}$ | 13.241                  |
|                                   | GZBL-Er   | 422.96                                 |                         | $^4S_{3/2} \rightarrow ^4I_{15/2}$ | 8.751                   |

Table 1. Absorption and emission photon numbers and enhanced percentage in the CZBL-Er and GCZBL-Er under the 979 nm laser excitation with different power densities.

Figure 7. (a,b) Dependence of up-conversion emission photon numbers on excitation powers in CZBL-Er and GCZBL-Er. (c,d) Quantum yields of CZBL-Er and GCZBL-Er under the 979 nm laser with different excitation power density.
CZBL-Er were identified utilizing a Shimadzu XRD-7000 diffractometer with Cu-Kα quench method in reducing atmosphere. In addition, 1.0 wt% ErF3 and 2.0 wt% YbF3 as dopants were introduced. Glass layers were prepared based on the molar host composition of 60ZrF4 and the adhesion of glass layers. Subsequently, all samples were annealed at 260 °C for 2 h, and then cooled down to room temperature inside the furnace. For optical measurements, the annealed samples were sliced into thin glass film on ceramic surface, net absorption power and net absorption photon number of GCZBL-Er exhibit an increase of ~10% by photon quantization in the integrating sphere. Corresponding the emission photon number and quantum yield enhance by 40% and 28%, respectively, and the higher photon release efficiency further implies the superiority of the special composite structure in light conversion. The high absorption-conversion efficiency attributed to the complex structure of transition layer confirms the macroscopical anti-escaping effect in GCZBL-Er, which provides a reliable approach for anti-NIR laser detection.

### Methods

#### Prototype design and fabrication of C_ZBL-Er and GC_ZBL-Er.

The fluoride ceramic-based composite glass layers were prepared based on the molar host composition of 60ZrF4–30BaF2–10LaF3 (ZBL) via the melt-quench method in reducing atmosphere. In addition, 1.0 wt% ErF3 and 2.0 wt% YbF3 as dopants were introduced into ZBL matrix and denoted as GCZBL-Er, and the individual glass phase and ceramic phase were labeled as G_ZBL-Er and C_ZBL-Er, respectively. The high-purity fluoride raw materials were melted at 900 °C for 5 min in a platinum crucible, and then the molten glasses were poured into a metal mold in a dry air atmosphere. Here, the lower liquid contacting with aluminum plate rapidly formed an ultrathin glass layer owing to the process of efficient heat conduction, where the metal mold quickly was taken away a lot of heat. Correspondingly, the upper liquid itself provided the energy needed for glass crystallization, which greatly promoted the formation of crystals in GCZBL-Er, which provides a reliable approach for anti-NIR laser detection.

#### Measurement and characterization.

The amorphous nature of G_ZBL-Er and the crystal structure of C_ZBL-Er were identified utilizing a Shimadzu XRD-7000 diffractometer with Cu-Kα radiation (λ = 1.5406 Å) operated at 40 kV and 30 mA. The morphological behaviors for the section of GCZBL-Er were observed by a field-emission scanning electron microscope (SEM instrument, JEOL JSM-7800F). The transmittance spectra of glass were recorded by Shimadzu Corporation UV3600 spectrophotometer, and diffuse reflectance spectra of samples were recorded by Shimadzu corporation UV3600 spectrophotometer, and

### Table 2. Quantum yields of C_ZBL-Er and GC_ZBL-Er excited by the 979 nm laser.

| Glasses          | QY of green emission (~550 nm) | QY of red emission (~650 nm) | Experimental method | References |
|------------------|--------------------------------|-----------------------------|---------------------|------------|
| Er3+ doped silicate glass | 2.0 × 10^-5 | —                           | Relative method     | 67         |
| Ho3+ doped NMAG  | 1.7 × 10^-4 | 24.1 × 10^-4               | Absolute method     | 68         |
| Er3+ doped NMAG  | 5.5 × 10^-5 | 21.9 × 10^-5               | Absolute method     | 68         |
| Er3+ doped BZYTLE (I) | 2.3 × 10^-4 | 1.4 × 10^-5               | Relative method     | 69         |
| Er3+ doped BZYTLE (II) | 3.3 × 10^-5 | 9.7 × 10^-5               | Relative method     | 69         |
| Ho3+ doped BALMF  | 6.3 × 10^-5 | 8.9 × 10^-5               | Absolute method     | 69         |
| Er3+ doped fluoride glasses | 1.0 × 10^-4 | —                           | Relative method     | 69         |
| Er3+ doped C_ZBL | 4.4 × 10^-5 | 4.0 × 10^-4               | Absolute method [This work] |            |
| Er3+ doped GC_ZBL | 5.8 × 10^-4 | 4.6 × 10^-4               | Absolute method [This work] |            |

### Table 3. Comparison of quantum yields for green and red emissions from Ho3+ and Er3+ in various glasses.

| Glasses          | Quantum yield (10^-5) | Enhanced percentage (%) |
|------------------|-----------------------|-------------------------|
|                  | 4I11/2 → 4I15/2       | 4I13/2 → 4I15/2         | 4F9/2 → 4I13/2 | Total |
| C_ZBL-Er         | 0.04                  | 0.37                    | 0.24             | 0.21 | 0.86 | 9.3 |
| GC_ZBL-Er        | 0.05                  | 0.41                    | 0.31             | 0.17 | 0.94 | 14.6 |
| C_ZBL-Er         | 0.12                  | 1.05                    | 0.73             | 0.50 | 2.40 | 14.6 |
| GC_ZBL-Er        | 0.15                  | 1.20                    | 0.91             | 0.59 | 2.85 | 14.6 |
| C_ZBL-Er         | 0.35                  | 2.53                    | 1.95             | 1.37 | 6.20 | 28.4 |
| GC_ZBL-Er        | 0.47                  | 3.27                    | 2.50             | 1.72 | 7.96 | 27.3 |
| C_ZBL-Er         | 0.47                  | 3.06                    | 2.35             | 1.67 | 7.55 | 27.2 |
| GC_ZBL-Er        | 0.66                  | 3.87                    | 3.06             | 2.02 | 9.61 | 27.3 |
| C_ZBL-Er         | 0.70                  | 3.78                    | 3.10             | 2.16 | 9.74 | 27.2 |
| GC_ZBL-Er        | 0.96                  | 4.91                    | 3.92             | 2.60 | 12.39 | 27.3 |
| C_ZBL-Er         | 0.89                  | 4.43                    | 4.00             | 2.42 | 11.74 | 25.0 |
| GC_ZBL-Er        | 1.24                  | 5.75                    | 4.62             | 3.06 | 14.67 | 25.0 |
The absolute spectral parameters of CZBL-Er and GCZBL-Er samples were measured in an integrating sphere of 3.3 inch inner diameter (Labsphere), which was connected to an exciting 979 nm NIR laser source and a QE65000 CCD detector (Ocean Optics) with 400μm-core and 600μm-core optical fibers, respectively. A standard halogen lamp (Labsphere, SCL-050) was adopted to calibrate this measurement system, and the spectral power distributions were obtained through fitting the factory data based on the black body radiation law.

Data availability

All data regarding the work presented here is available upon reasonable request to the corresponding author.

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Author contributions
H.F. Shi and H. Lin conceived and designed the experiments. H.F. Shi, P.J. Lin and J.X. Yang carried out most of the experiments and data analysis. H.F. Shi, P.J. Lin, I.X. Yang, J.L. Yuan, E.Y.B. Pun, Y. Song, X. Zhao and H. Lin discussed the results and commented on the manuscript. H.F. Shi, P.J. Lin and J.X. Yang wrote and revised the manuscript.
Competing interests
The authors declare no competing interests.

Additional information
Correspondence and requests for materials should be addressed to X.Z. or H.L.

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