Broadening and enhancing 2.7 μm emission spectra in Er/Ho co-doped oxyfluoride germanosilicate glass ceramics by imparting multiple local structures to rare earth ions

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Er/Ho co-doped oxyfluoride germanosilicate glass and glass ceramics are prepared and compared. The results indicate that the glass consists of SiO4 and GeO4 structural units, while the network of the glass ceramics consists of SiO4, GeO4, and GeO6 units together with NaYF4 nanocrystals. The presence of multiple local structures in glass ceramics creates a range of dipole environments, which is beneficial to the broadening of 2.7 μm emission. Two other reasons are attributed to the broadening of 2.7 μm emission in glass ceramics: the energy-level splitting of Er3+/0.135 and the enhancement of the Ho3+/0.135:5I6 → 5I7 transition in NaYF4 nanocrystals.

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1. INTRODUCTION

Lasers in the mid-infrared region, covering the 2 to 5 μm wavelengths, are of great interest in scientific research and practical applications [1–3]. Specifically, broadband tunable mid-infrared lasers have widespread applications. For example, molecular species such as HF, H2O, CO, and CO2, have high absorption cross sections in this spectral range [4], and hence a broadband mid-infrared region laser exhibits promising applications in highly sensitive chemical analysis. Laser transitions of rare-earth (RE) cations that generate emissions in the range of 3 μm include the 4I11/2 → 4I13/2 transition of Er3+, the 5I6 → 5I7 transition of Ho3+, and the 6H13/2 → 6H15/2 transition of Dy3+. Considerable effort has been made towards pursuing suitable host materials for the mid-infrared spectral region in recent decades. Mid-infrared emissions are readily vulnerable to multiphonon relaxation that can only be achieved in host materials with low phonon energy. To date, several glass materials have been proposed as candidates for mid-infrared fibers, including oxyfluoride glass ceramics [5], germanate [6], tellurite [7], fluoride [8], and chalcogenide glasses [4]. Here, it is worth noting that oxyfluoride glass ceramics combine the advantages of the low-phonon-energy environment of fluoride nanocrystals (NCs) and excellent macroscopic properties of an oxide glass matrix [9–11]. Therefore, they are considered efficient and promising materials for mid-infrared laser output. In our previous work [12], we demonstrated that oxyfluoride silicate glass ceramics have better mid-infrared emission properties than corresponding glass materials.

In glasses, the structure of the cationic sites is not strictly fixed and can show differences in the angle and distance bonds to the surrounding anions, which determines inhomogeneous broadening of the spectral lines [13]. Furthermore, in GeO2- and TeO2-based glasses in which more than one structural unit exists, a range of dipole environments are created for RE ions that are ideal for obtaining broadband spectra [14]. We [15] and others [16] have proved that silicate glass with proper GeO2 can provide broadband emission spectra. Therefore, we expect to be able to acquire broadband emission spectra in oxyfluoride germanosilicate glass ceramics by enabling a rare-earth dopant to distribute in multiple local structures including SiO4 tetrahedron, GeO4 tetrahedron, and fluoride NCs, etc.

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Furthermore, the partial additions of GeO₂ at the expense of SiO₂ in oxyfluoride silicate glass ceramics can decrease their maximum phonon energy and improve their refractive index, which is beneficial to attaining higher absorption and emission cross sections of mid-infrared emissions [14]. What’s more, the reports involving oxyfluoride germanosilicate glass ceramics are very few, and it is interesting to investigate the complicated glass structure and corresponding mid-infrared emission properties.

In this work, a series of Er/Ho co-doped oxyfluoride germanosilicate glass and glass ceramic samples containing NaYF₄ NCs are prepared. The NaYF₄ NCs are characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The glass structure is investigated by Fourier-transformed infrared (FTIR) spectra. Upconversion and mid-infrared emission properties and a corresponding energy transfer mechanism in glass and glass ceramics are discussed. Additionally, the energy transfer coefficients of Er³⁺:A¹I₇/₂ → Ho³⁺:I₆ and Er³⁺:I₃/₂ → Ho³⁺:I₇ are both calculated to understand the change in emission properties.

2. EXPERIMENT

Glass with composition of 25SiO₂–25GeO₂–15Al₂O₃–15Na₂O–10NaF–9.2YF₃–0.5ErF₃–0.3HoF₃ (named SGG) was prepared by the melt-quenching method, starting from analytical-grade raw materials in powder form. The raw materials with required proportion were mixed homogeneously and put into a covered corundum crucible in order to prevent the vaporization of fluoride. Then the crucible was placed in an elevator furnace at 1450°C, where it remained for half an hour. After melting, the glass was quenched on preheated stainless steel plates before being annealed at 450°C for 2 h to release inner stress. A fraction of each sample was ground.

Transparent oxyfluoride glass ceramics were obtained from the precursor glasses by thermal treatment method. The precursor glasses were put into an oven at 600°C, 620°C, 640°C, and 660°C (named SGG) was devitrified. Importantly, the thermal stability parameter of heat treatment temperature ranging from 600°C to 640°C has no obvious influence on the type of the crystalline phase in glass. All XRD curves of the glass ceramic samples presented sharp characteristic peaks in the same position, corresponding to the α-NaYF₄ crystalline phase (JCPDS No. 060342). The results also indicate that the change of heat treatment temperature ranging from 600°C to 640°C has no obvious influence on the type of the crystalline phase in the glass ceramic. However, the diffraction peaks of samples heated to 600°C, 620°C, and 640°C are gradually stronger, indicating that the size of NaYF₄ crystal becomes larger as the heat treatment temperature rises. The inset of Fig. 2(a) shows the prepared samples (from left: SGG, SGGC1, SGGC2, and SGGC3) in daylight. It is seen that the first three samples show high transparency, but the SGGC3 sample is a little opaque.

3. RESULTS AND DISCUSSION

A. Differential Thermal Analysis

The DSC curve of the SGG sample is represented in Fig. 1. The glass transition temperature $T_g$ of the glass appears around 500°C. The weak exothermal peak around 620°C represents the crystallization of fluoride component of the glass matrix, while the strong exothermal peak around 736°C corresponds to the crystallization of germanosilicate oxides of the glass matrix. The heat treatment temperature was thus selected as 600°C, 620°C, 640°C, and 660°C. To prevent the RE ions from entering fluoride NCs and resulting in narrow emission spectra, the heat treatment duration cannot be too long and was 2 h in our case. The glass ceramic sample heated to 660°C was devitrified. Importantly, the thermal stability parameter $T_{x2} - T_g = 201°C$ (where $T_{x2}$ represents the onset crystallization temperature corresponding to the second exothermal peak in the DSC curve) is high, which is favorable for the glass fiber drawing.

B. Morphological Characteristics

The X-ray diffraction patterns for glass and glass ceramic samples are shown in Fig. 2(a). The absence of any sharp crystallization peak in the XRD curve of the SGG sample is owing to the amorphous structural nature of glass. All XRD curves of the glass ceramic samples presented sharp characteristic peaks in the same position, corresponding to the α-NaYF₄ crystalline phase (JCPDS No. 060342). The results also indicate that the change of heat treatment temperature ranging from 600°C to 640°C has no obvious influence on the type of the crystalline phase in glass ceramic. However, the diffraction peaks of samples heated to 600°C, 620°C, and 640°C are gradually stronger, indicating that the size of NaYF₄ crystal becomes larger as the heat treatment temperature rises. The inset of Fig. 2(a) shows the prepared samples (from left: SGG, SGGC1, SGGC2, and SGGC3) in daylight. It is seen that the first three samples show high transparency, but the SGGC3 sample is a little opaque. What’s more, it can be found that the diffraction peaks present a slight shift to large angle, owing to lattice contraction resulting from the partial substitution of Y³⁺ ions (radius 1.015 Å) with Er³⁺ ions of smaller radius (1.00 Å) [17].

![Fig. 1. DSC curve of oxyfluoride germanosilicate glass.](image-url)
This result is important because it indicates that the distribution of rare earth ions in glass and NCs can be controlled by altering heat treatment temperature, which is the precondition of the tuning of spectral bandwidth. To get further insight into the size, morphology, and distribution of NaYF₄ NCs in glass matrix, a TEM image of the SGGC2 sample is shown in Fig. 2(b). It is evident that spherical NCs, mainly sized 40–55 nm [see Fig. 2(c)], are homogenously distributed in the glass matrix.

### C. Structural Analysis

The density measurement of glass and glass ceramics can give a rough macroscopic overview of the change in structural packing. The density of the SGG, SGGC1, SGGC2, and SGGC3 samples is 3.053, 3.076, 3.077, and 3.079 g/cm³, respectively. The increased density suggests a more compact glass structure in glass ceramic, which can be attributed to the structure-ordered crystallization process. Figure 3 illustrates the FTIR absorption spectra of the oxyfluoride germanosilicate glass and glass ceramics. FTIR spectroscopy is able to obtain essential information concerning the arrangement of the structural units in the glass materials. The bands at around 435 and 1000 cm⁻¹ are corresponding to Si-O-Si bending vibration and asymmetric stretching, respectively [18]. The band near 880 cm⁻¹ is assigned to Ge-O-Ge asymmetric stretching vibration in the GeO₄ tetrahedral unit, while the band close to 695 cm⁻¹ is assigned to Ge-O-Ge stretching vibration in GeO₆ units [19,20], which was not observed in the glass sample. This suggests that the heat treatment induces some Ge⁴⁺ cations to incorporate in the glass ceramic network as GeO₆ units. It can be explained that the generation of bridging oxygen in glass matrix, accompanied by the crystallization of NaYF₄ NCs, leads to the transformation from GeO₄ to GeO₆ units. Therefore, it can be concluded that the glass network consists of SiO₄ and GeO₄ structural units while the network of the glass ceramics consists of SiO₄, GeO₄, and GeO₆ units.

### D. Absorption Spectra

Figure 4(a) presents the absorption spectra of all prepared samples. Typical absorption bands attributed to Er³⁺ and Ho³⁺ ions’ transitions from ground state to excited state levels were observed and labeled. The ultraviolet absorption cutoff wavelength of the SGGC3 sample exhibits an obvious redshift owing to the light-scattering phenomenon in the translucent SGGC3 sample. In addition, as shown in Fig. 4(b), weak Stark split peaks appear in the 1.53 μm absorption band in SGGC samples at around 1560 nm due to the crystal field effect. In the case of Er³⁺, the transitions ⁴Ι₁₅/₂ → ⁵Η₁₁/₂ and ⁴Ι₈/₂ → ⁵Η₁₂/₂.
$^4I_{13/2} \rightarrow ^4G_{11/2}$ are hypersensitive, and are sensitive to small changes of local environment around Er$^{3+}$. The oscillator strengths of the $^4I_{13/2} \rightarrow ^4G_{11/2}$ transition of the SGG and SGGC2 samples are 7.092 and 5.993, respectively. Lower oscillator strength in the glass ceramic sample may be due to the higher-inhomogeneity environment in glass compared with NaYF$_4$ NCs in the SGGC2 sample [21].

**E. Emission Spectra and Emission Cross Section**

As revealed by the structural analysis of glass and glass ceramics, the germanosilicate glass ceramic can provide multiple local structures for RE ions. The local environment of RE ions in such glass ceramics containing complicated structure, in fact, was determined by heat treatment condition. For example, the distribution of RE ions in glass ceramics was affected by heat treatment temperature. The increased heat treatment temperature facilitated the incorporation of RE ions into fluoride NCs, and can make the RE ions distribute in multiple local structures easily. In order to reveal the influence of altering heat treatment temperature on the fluorescence behavior of glass ceramic, upconversion and 2.7 μm emission spectra were all measured under 980 nm laser diode excitation. As depicted in Fig. 5(a), intense green and red upconversion emissions of Er$^{3+}$ and Ho$^{3+}$ are obtained in glass ceramics while they are weak in glass. The significant enhancement of upconversion emissions from Er$^{3+}$ and Ho$^{3+}$ ions is attributed to the incorporation of Er$^{3+}$ and Ho$^{3+}$ ions into NaYF$_4$ NCs, which provides a low-phonon-energy environment. In addition, a Stark split of 656 nm upconversion emission due to energy level splitting in the crystal field is also observed in all SGGCs while it does not occur in the SGG; this is also observed in other glass ceramic systems [22,23]. The mid-infrared emission spectra in the samples were measured to identify targeted broadening of spectra in germanosilicate glass ceramics. As shown in Fig. 5(b), the full width at half-maximum (FWHM) of the 2 μm emission spectrum is close to 178, 186, 190, and 192 nm for the SGG, SGGC1, SGGC2, and SGGC3 samples, respectively. On the other hand, as shown in Fig. 5(c), the FWHM of the 2.7 μm emission spectrum is close to 140, 164, 154, and 172 nm for the SGG, SGGC1, SGGC2, and SGGC3 samples, respectively.

The results confirm that the broadening of the mid-infrared emission spectra is achieved in the designed glass ceramics. In addition, the intensity of the 2.7 μm emission was enhanced at first, with the increase of heat treatment temperature; however, it decreased when the temperature further increased from 620°C to 640°C. The decreased 2.7 μm emission of Er$^{3+}$ ions was attributed to enhanced upconversion emission of Er$^{3+}$ ions. In this case, the intensity change of the mid-infrared emission of RE ions in low-phonon-energy environment would be related to RE ion concentration. Further, it can be found that the 2.7 μm emission spectrum of the SGG sample is basically a Gaussian peak while the 2.7 μm emission spectra of the SGGC samples have two small bulges at around 2640 and 2800 nm compared with the former, which will be explained in next section. Furthermore, as shown in the inset of Fig. 5(d), the lifetime of $^4I_{11/2}$ level in the SGGC2 sample was as high as 2.51 ms, which is beneficial to obtaining 2.7 μm laser output. Based on these discussions, it can be concluded that the influence of heat treatment temperature on mid-infrared emission in SGGCs is complicated due to the distribution of RE ions in glass ceramics and possibly changed energy transfer. The involved energy transfer will be discussed later.

**Fig. 5.** (a) Visible upconversion emission spectra, (b) 2 μm emission spectra, (c) 2.7 μm emission spectra, and (d) 2.7 μm emission cross section and decay curve of $^4I_{11/2}$ level (inset) in the SGGC2 sample.
To evaluate the potential applications of glass ceramic in mid-infrared host materials, the 2.7 μm emission cross section of the SGGC2 sample was calculated by the Füchtbauer–Ladenburg equation:

\[ \sigma_{\text{em}}(\lambda) = \frac{\lambda^2 \sigma_{\text{rad}}}{8\pi c n_0^2} \int \frac{J(\lambda)}{\lambda^2} d(\lambda), \]

where \( \lambda \) is the wavelength, \( J(\lambda) \) is the fluorescence intensity, and \( c \) and \( n \) are the light speed and index of refraction (here, the value is 1.532), respectively. The spontaneous radiative transition probability \( \sigma_{\text{rad}} \) was obtained based on measured absorption spectra and Judd–Ofelt theory [24,25]. In view of the fact that the Er\(^{3+}\):I\(_{11/2} \rightarrow \)4I\(_{13/2} \) transition was much stronger than the Ho\(^{3+}\):I\(_{11/2} \rightarrow \)3I\(_{2} \) transition in present glass ceramics, the \( \sigma_{\text{rad}} \) (22.91 s\(^{-1}\)) used here is the spontaneous radiative probability of Er\(^{3+}\):I\(_{11/2} \rightarrow \)4I\(_{13/2} \) transition. The calculated result is plotted in Fig. 5(d), and one can find that the peak emission cross section at 2.7 μm is 5.0 × 10\(^{-21}\) cm\(^2\), which is comparable to Er\(^{3+}\):doped ZBLAN glass (5.7 × 10\(^{-21}\) cm\(^2\)) [26]. Combined with the high emission cross section and broadband spectra at 2.7 μm, oxyfluoride germanosilicate glass ceramic may be a promising and competitive candidate for mid-infrared tunable laser host materials.

F. Energy Transfer Mechanism

The more complicated glass network in glass ceramic creates a range of dipole environments, which may explain the broadening of the 2 μm emission spectra. However, there are more reasons for the change in 2.7 μm emission spectra in SGGCs. Understanding the energy transfer mechanism of RE ions is beneficial to comprehending the reason for enhancing and broadening the 2.7 μm emission in SGGCs. On the basis of measured emission spectra and previous reports [8,27,28], an energy-level diagram of Er\(^{3+}\) and Ho\(^{3+}\) is depicted in Fig. 6 and the energy transfer mechanism of Er\(^{3+}\) and Ho\(^{3+}\) ions is proposed as follows.

First, the ions at the ground state Er\(^{3+}\):4I\(_{11/2} \) level absorb energy from the pump source (980 nm LD) and are excited to the 4I\(_{13/2} \) level.

On one hand, the ions at the Er\(^{3+}\):4I\(_{11/2} \) level can not only transfer energy to the Ho\(^{3+}\):I\(_{6} \) level (ET1:Er\(^{3+}\):4I\(_{11/2} + \)Ho\(^{3+}\):I\(_{6} \rightarrow \)Ho\(^{3+}\):4I\(_{15/2} \) + Er\(^{3+}\):4I\(_{13/2} \)), but they can also decay to the Er\(^{3+}\):4I\(_{13/2} \) level by nonradiative decay or radiative transition (Er\(^{3+}\):4I\(_{11/2} \rightarrow \)Er\(^{3+}\):4I\(_{13/2} + 2.7 \) μm). Then, the ions at the Er\(^{3+}\):4I\(_{13/2} \) level can transfer energy to the Ho\(^{3+}\):I\(_{5} \) level (ET2:Er\(^{3+}\):4I\(_{13/2} + \)Ho\(^{3+}\):I\(_{5} \rightarrow \)Ho\(^{3+}\):4I\(_{15/2} \) + Er\(^{3+}\):I\(_{13/2} \) + Er\(^{3+}\):I\(_{15/2} \)) due to small energy gap between them. The ions at the Ho\(^{3+}\):I\(_{5} \) level can radiate energy to the ground state Ho\(^{3+}\):I\(_{6} \) level, generating 2 μm light emission.

On the other hand, the ions at the Er\(^{3+}\):4I\(_{11/2} \) level can absorb 980 nm photon energy and are excited to a higher Er\(^{3+}\):F\(_{7/2} \) level, which nonradiatively decays subsequently to lower excited energy levels. The ions at the excited energy levels of Er\(^{3+}\) can not only transfer energy to adjacent excited energy levels of Ho\(^{3+}\) (i.e., ET3:Er\(^{3+}\):H\(_{11/2} \) + Ho\(^{3+}\):I\(_{6} \rightarrow \)Ho\(^{3+}\):F\(_{4} \) + Er\(^{3+}\):4I\(_{15/2} \)), but they can also radiate their energy to the ground state Er\(^{3+}\):I\(_{15/2} \) level, generating upconversion emissions (i.e., 524, 544, 656, 668 nm, etc.). Similarly, the ions at the excited energy levels of Ho\(^{3+}\) can generate light emissions (i.e., 551, 656 nm, etc.) by radiative transition. The ions at the Er\(^{3+}\):4I\(_{11/2} \) level easily decay nonradiatively to lower levels in high phonon energy environments, and therefore the energy transfer processes mentioned in this paragraph mainly happen in NaYF\(_{4}\) NCs.

Thus, we can conclude that the 668 nm emission in glass ceramics originates from the transition between the splitting energy level of Er\(^{3+}\):F\(_{7/2} \) and the ground state Er\(^{3+}\):I\(_{15/2} \) level. In addition, the change in peak shape of 2.7 μm spectra can be attributed to the energy level splitting of Er\(^{3+}\) in the crystal field (bulge at 2640 nm) and the enhancement of Ho\(^{3+}\):I\(_{6} \) → 3I\(_{2} \) transition (bulge at 2800 nm). It is noted that the energy level splitting of Er\(^{3+}\):I\(_{15/2} \) reflected in the 2.7 μm emission spectra has a good agreement with the results of the absorption spectra, as shown in the inset of Figs. 4(b) and 5(c).

However, the origins of decreased 2 μm emission and enhanced 2.8 μm emission of Ho\(^{3+}\) in glass ceramic are still unclear, which can be revealed by further non-resonant energy transfer analysis between Er\(^{3+}\) and Ho\(^{3+}\) in the next section.

G. Non-Resonant Energy Transfer Analysis

In order to broaden the mid-infrared spectra around 2.7 μm, it is necessary for Er\(^{3+}\) to transfer some energy to Ho\(^{3+}\), which can generate 2.8 μm (close to 2.7 μm) emission through I\(_{6} \rightarrow \)I\(_{5} \) radiative transition. Although the SGG sample with high phonon energy can promote energy transfer from Er\(^{3+}\) to Ho\(^{3+}\) with the assistance of fewer phonons, it also leads to high multi-phonon relaxation rates and weakens the mid-infrared emissions. Hence, it is necessary to quantitatively investigate the energy transfer process further, which can be evaluated by the calculations of the absorption and emission cross sections of Er\(^{3+}\) and Ho\(^{3+}\) ions using Dexter theory [29]. When phonon assistance is taken into consideration, the Dexter expression for the energy transfer coefficient (\( C_{DA} \)) by dipole–dipole mechanism can be expressed as

\[
C_{DA} = \frac{6c\sigma_{\text{em}}(\lambda_{D})\sigma_{\text{abs}}(\lambda_{D})}{(2\pi)^{2}\varepsilon_{0}^{2}n_{m}^{2}} \sum_{n=0}^{\infty} e^{-(2n+1)s_{0}} \frac{S_{n}^{m}}{m!} (n + 1)^{m}
\times \int \sigma_{\text{em}}(\lambda_{D})\sigma_{\text{abs}}(\lambda_{D})d(\lambda),
\]

where \( c \) is the light speed in vacuum, \( n \) is the refractive index of the medium, and \( \sigma_{\text{em}}(\lambda_{D}) \) and \( \sigma_{\text{abs}}(\lambda_{D}) \) are the degeneracy of the lower and upper levels of the donor (here, Er\(^{3+}\)), respectively. \( h\omega_{0} \) is

![Fig. 6. Energy level diagrams and energy transfer mechanism from Er\(^{3+}\) to Ho\(^{3+}\).](image-url)
the maximum phonon energy (here, 1050 and 300 cm⁻¹ were used for glass and NaYF₄ NCs, respectively) [30], \( \bar{v} \) is the average occupancy, \( m \) is the number of phonons participating in the energy transfer, \( S_0 \) is the Huang–Rhys factor (0.31 for RE ions), and \( \lambda_{+}^{\text{m}} = 1/(1/\bar{v} - \text{m} \bar{v} \text{h} \omega) \) is the wavelength with \( \text{m} \) phonon creation. In the SGGC2 sample, \( C_{DA} \) is calculated for rare earth ions distributed both in glass and NaYF₄ NCs. The absorption and emission cross sections of Er³⁺ and Ho³⁺ ions in the SGG and SGGC2 samples are calculated based on measured absorption spectra and the McCreery formula [31], which are presented in Fig. 7. It can be seen that the ET1 process for energy transfer between Er³⁺ and Ho³⁺ ions in SGG sample, significantly lower than that in SGGC2 sample, which indicates that the ET1 process is more efficient in germanosilicate glass ceramic. The calculation results also show that the ET2 process is more efficient in glass. The absorption cross section of Er³⁺ does not overlap with the absorption cross section of Ho³⁺ in both glass and glass ceramic samples. Therefore, the ET1 process is more efficient in germanosilicate glass ceramic. The ET2 process is more efficient in glass ceramic.

For the ET1 process, three or four phonons are needed to fill the energy gap between \( \text{Er}^{3+} \cdot \text{I}_{13/2} \rightarrow \text{Er}^{3+} \cdot \text{I}_{15/2} \) emission and \( \text{Ho}^{3+} \cdot \text{I}_{8} \rightarrow \text{Ho}^{3+} \cdot \text{I}_{6} \) absorption in NaYF₄ NCs. However, only one phonon is required for the ET2 process in glass. The calculation results also show that the \( C_{DA} \) of the ET2 process is 1.88 × 10⁻⁴¹ cm² in NaYF₄ NCs embedded in SGGC2 sample, significantly lower than that in SGG sample (11.75 × 10⁻⁴¹ cm²) and SGGC2 glass matrix (10.08 × 10⁻⁴¹ cm²). These results indicate that the ET2 process is more efficient in germanosilicate glass ceramic than in NaYF₄ NCs, which can explain the decrease of 2 μm emission in glass ceramic.

For the ET1 process, three or four phonons are needed to fill the energy gap between \( \text{Er}^{3+} \cdot \text{I}_{11/2} \rightarrow \text{Er}^{3+} \cdot \text{I}_{11/2} \) emission and \( \text{Ho}^{3+} \cdot \text{I}_{8} \rightarrow \text{Ho}^{3+} \cdot \text{I}_{6} \) absorption in NaYF₄ NCs. However, only one phonon is required for the ET1 process in glass. The calculation results also show that the \( C_{DA} \) of the ET1 process is 0.44 × 10⁻⁴¹ cm² in NaYF₄ NCs embedded in SGGC2 sample, significantly lower than that in SGG sample (1.10 × 10⁻⁴¹ cm²) and SGGC2 glass matrix (1.25 × 10⁻⁴¹ cm²). These results indicate that the ET1 process is stronger than the ET2 process for energy transfer between Er³⁺ and Ho³⁺ ions.

4. CONCLUSION

In summary, Er/Ho co-doped oxyfluoride germanosilicate glass and glass ceramic containing NaYF₄ NCs were prepared. Differential thermal analysis indicates the germanosilicate glass has good thermal stability. Transmission electron microscopy and X-ray diffraction demonstrate that both the formation of NaYF₄ NCs during the heat treatment processes and the increase of heat treatment temperature can accelerate the growth of NaYF₄ NCs, together with the incorporation of more RE ions. The glass network consists of SiO₄ and GeO₄ structural units, while the network of the glass ceramics consists of SiO₄, GeO₄, and GeO₄ units together with NaYF₄ NCs. Therefore, RE ions can locate at multiple local structures in oxyfluoride germanosilicate glass ceramics.

Absorption spectra were measured and the results indicate that the formation of NaYF₄ NCs has an influence on the hypersensitive transitions and \( \text{Er}^{3+} \) absorption in NaYF₄ NCs. Upconversion emissions were significantly enhanced, and Stark split of green emission occurred in glass ceramic samples. Broadening of 2 and 2.7 μm emission spectra, together with the change in spectra shape, were observed in oxyfluoride germanosilicate glass ceramics. Analyses were conducted of the energy transfer mechanism between Er³⁺ and Ho³⁺ and the non-resonant energy transfer to comprehend the change in fluorescence spectra. The results indicate that the reasons for the broadening of the 2.7 μm emission spectra in SGGs are: (1) more complicated glass network, (2) energy level splitting of Er³⁺ in crystal field, and (3) the enhancement of \( \text{Ho}^{3+} \cdot \text{I}_{6} \rightarrow \text{I}_{7} \) transition in NaYF₄ nanocrystals. The calculation of \( C_{DA} \) for the ET2 process can explain the decreased 2 μm emission and indicate the origin of enhanced 2.8 μm emission in glass ceramic.

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![Fig. 7. Absorption and emission cross sections of Er³⁺ and Ho³⁺ in (a) SGG glass and (b) SGGC2 sample.](image-url)


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