Up-conversion luminescence properties and energy transfer of Er^{3+}/Yb^{3+} co-doped oxyfluoride glass ceramic containing CaF_2 nano-crystals*

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The Er^{3+}/Yb^{3+} co-doped transparent oxyfluoride glass-ceramics containing CaF_2 nano-crystals were successfully prepared. After heat treatments, transmission electron microscopy (TEM) images showed that CaF_2 nano-crystals of 20–30 nm in diameter precipitated uniformly in the glass matrix. Comparing with the host glass, high efficiency upconversion luminescence of Er^{3+} at 540 nm and 658 nm was observed in the glass ceramics under the excitation of 980 nm. Moreover, the size of the precipitated nano-crystals can be controlled by heat-treatment temperature and time. With the increase of the nano-crystal size, the intensity of the red emission increased more rapidly than that of the green emission. The energy transfer process of Er^{3+} and Yb^{3+} was convinced and the possible mechanism of Er^{3+} up-conversion was discussed.

Keywords: nano-crystals, up-conversion luminescence, Er^{3+}/Yb^{3+} co-doped glass ceramics

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1. Introduction

Up-conversion luminescent materials doped with rare earth (RE) ions play an important role in numerous potential applications such as infrared pumped visible eye-safe lasers, three-dimensional display, optical data storage, and medical diagnostics.[1–5] However, the enhancement of the up-conversion luminescence efficiency is still a key problem blocking their practical applications. Consequently, numerous methods, such as doping with sensitization ions or selecting one kind of low phonon energy glass host, have been tried for improving the excitation efficiencies and enhancing the up-conversion luminescence.

In recent years, oxyfluoride glass ceramics come to our attention as up-conversion host materials because they not only have high chemical and mechanical stabilities similar to the oxides, but also have low phonon energies related to the fluorides. In 1970s, the oxyfluoride glass ceramics were first produced by further heat treatments of the prepared glass above the glass transition temperature.[6] The doped rare-earth ions can be selectively concentrated in the precipitated fluorite glass ceramics, and in this way the up-conversion luminescence is increased owing to the low energy phonon environment and the shortened distance between the ions. The discussion was sequentially identified in Wang and Ohwaki's research,[7] reporting the efficient infrared to green up-conversion of Er^{3+} ions in a transparent oxyfluoride glass ceramic. The up-conversion luminescence of the glass ceramic was found to be much stronger than that of the YbF_3 or ErF_3 singly doped fluoride glasses, meaning that the sensitization of this nano-composite with Yb^{3+} ions may be a good choice due to the efficient energy transfer from Yb^{3+} to Er^{3+} ions.[8,9] The increase of the up-conversion luminescence of the Er^{3+}/Yb^{3+}co-doped transparent oxyfluoride glass ceramic is obvious in cubic $NaYF_4$,[10–12] $Ca_5(PO_4)_3F$,[13] Ba_2GdF_7,[14] CaF_2,[15,16] PbF_2,[17] YF_3,[18,19] $LiYbF_4$,[20] LaF_3,[21] and CeF_3.[22] Among them, the CaF_2 crystal is an important optical raw material with high solubility of both sensitizer and activator RE ions. It is a good material due to its high solubility of both activator and rare earth ions and strong ability of keeping the glass transparent.[23]

Previous research is almost always concentrated on the improvement of the up-conversion luminescence, but the size and morphology of nano-crystals and their influences on the rare earth up-conversion have not been discussed a great deal. In this paper, the relationship between crystallization characteristics and the up-conversion luminescence in Er^{3+}/Yb^{3+} co-doped oxyfluoride glass-ceramics under 980 nm excitation is investigated after we have successfully prepared the glass ceramics containing CaF_2 nano-crystals doped with Er^{3+} and Yb^{3+} ions. Furthermore, the different raising tendencies of up-conversion luminescence in the red and the green emission parts are discussed, and the mechanism for the Er^{3+} up-conversion emission is proposed.

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2. Experiment

The samples were prepared with the following composition (in mol%): 50 SiO_2–20 Al_2O_3–30 CaF_2–0.5 ErF_3 – xYbF$_3$–$(9.5-x)$GdF$_3$ (x = 0, 1, 3, 5, 7, 9). For each group, about 10 g of chemical materials were mixed and melted in a covered alumina crucible at 1400 °C for about 30 min. Then the glasses were quenched onto a preheated stainless steel mold. The glass transition temperature (T_g = 614 °C), the onset of the crystallization temperature (T_x = 701 °C), and the bulk crystallization temperature (T_c = 884 °C) were determined using differential thermal analysis (DTA, DTA-60AH, SHIMADZU) at a heating rate of 10 °C/min. The quenched samples were heat treated at 530 °C for 4 h and cooled down slowly to room temperature. Then, the samples were cut into sizes of 10 mm × 10 mm × 2 mm and surface-polished for optical measurements. The samples were further heated at 680 °C for 4 h to introduce crystallization and form transparent glass ceramics. The corresponding glass ceramics are named as 0GC, 1GC, 3GC, 5GC, 7GC, and 9GC, respectively, according to their Yb^{3+} contents. The samples were also heated at 680 °C for different hours. The corresponding glass ceramics are named as GC4, GC6, GC8, GC10, and GC12, respectively, according to the further heated hours.

The formation of CaF_2 crystal phase was confirmed by using X-ray diffraction (XRD, Bruker D8-Advance diffractometer using Cu $K\alpha$ ($\lambda = 1.54$ Å) radiation). The microstructures of the samples were studied using transmission electron microscopy (TEM, JEM-2100). The fluorescence spectra were measured using a spectrophotometer in the wavelength range from 350 nm to 750 nm (Spectrophotometer F-7000; Hitachi Ltd.) with a 980 nm laser diode as the excitation source.

3. Results and discussion

As reported in the previous work of our group, CaF_2 nano-crystals can be precipitated from the oxyfluoride glass matrix during the heat treatment process. Therefore, it is necessary to research on the behaviors of the fluoride glass ceramic. Firstly, the thermodynamic property of the Er^{3+}/Yb^{3+} co-doped oxyfluoride glass is investigated (Fig. 1).

As can be seen in Fig. 1, three exothermic peaks are observed in the DTA curve of the sample doped with 0.5 mol% ErF_3 and 1 mol% YbF_3. Except the glass transition peak at temperature T_g (614 °C) and the first crystallization peak at T_c (884 °C), an additional exothermic peak appears between T_g and T_c. The result means that microcrystals may be precipitated from the glass matrix when heating at the temperature of T_x. As imagined, the above glass sample is heated at about 680 °C for 4 h, then the structure of the glass is investigated, which is shown in Fig. 2.

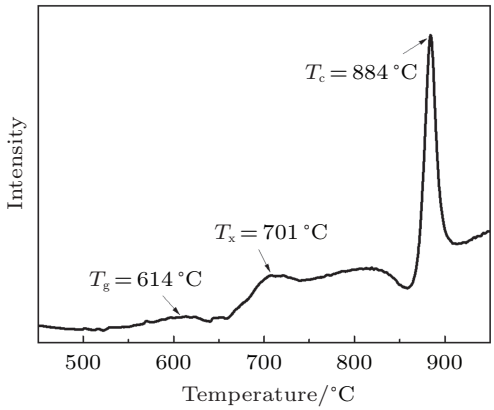


Fig. 1. DTA curve of the 50 SiO_2–20 Al_2O_3–30 CaF_2–0.5 ErF_3–1 YbF_3–8.5 GdF_3 glass as prepared.

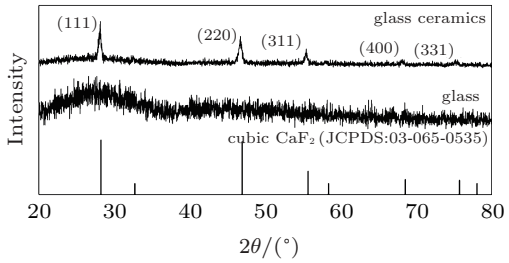


Fig. 2. XRD patterns of the as-prepared glass, 1GC, and the standard cubic CaF_2 phase.

Figure 2 shows the XRD patterns of the host glass and the glass after heat treatment at T_x for comparison, the reference crystal XRD pattern (CaF_2, JCPDS: 03-065-0535) is also illustrated here. One can clearly see that the as-prepared glass presents the amorphous phase with no obvious diffraction peaks. While after the sample has been heat treated, a series of significant diffraction peaks appear and they can be easily attributed to the referenced cubic CaF_2 phase. Additionally, no other peaks can be found in the XRD pattern, revealing that the products are basically of pure CaF_2 phase. According to the Scherrer equation, the CaF_2 nano-crystals are about 20.7 nm. In order to prove the CaF_2 nano-crystals precipitated during the heat-treatment process, TEM and energy-dispersive X-ray spectroscopy (EDX) measurements were carried out, which are shown in Fig. 3.

The TEM micrograph of the CaF_2 nano-crystals in 0.5 mol% Er^{3+}–1.0 mol% Yb^{3+} doped sample after heat treatment is displayed in Fig. 3(a). It is noticed that many spherical CaF_2 nano-crystals are precipitated in the glass matrix and distribute homogenously with a size of about 20–30 nm, which is in good agreement with the size calculated with the Scherrer equation. Furthermore, in the high-resolution TEM (HRTEM) image, the lattice fringes on the individual CaF_2 nano-crystals are clearly distinguished, indicating the high integrity of the crystal structure. In Fig. 3(b), the compositional analysis of an individual particle by EDX demonstrates the dominating

presence of Ca, F, Er, and Yb elements, which further confirms that the nano-crystals are in the CaF_2 phase and meanwhile, $Er^{3+}$and Yb^{3+} ions are mainly concentrated in the CaF_2 nano-crystals. In addition, the Al, Si, and O elements are attributed to the glass matrix surrounding the nano-crystals. It is well known that the addition of sensitizer ions can help the enhancement of the rare earth up-conversion luminescence by the energy transition to the activators. In the presence of microcrystalline, typical Er^{3+}/Yb^{3+} co-doped up-conversion luminescence spectra of six samples were measured with excitation source at 980 nm and are shown in Fig. 4.

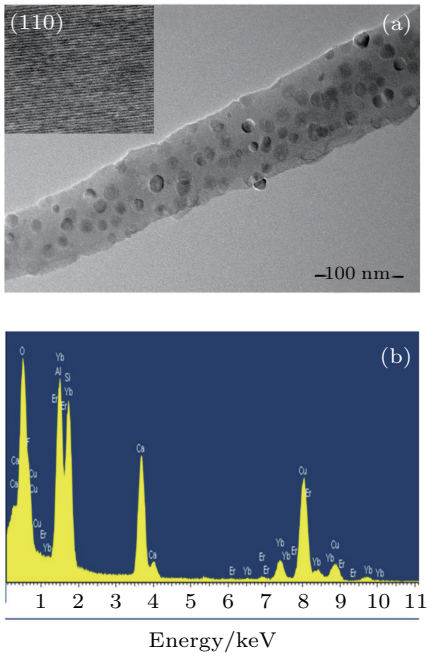


Fig. 3. (color online) (a) TEM micrograph of 1GC and the HRTEM image of an individual CaF_2nano-crystal. (b) EDX spectrum of an individual CaF_2 crystal from the glass matrix.

As can be seen in Fig. 4(a), with the increase of the sensitizer Yb^{3+} content, the Er^{3+} up-conversion is increased significantly and finally quenches at 7 mol% Yb^{3+} doping. The emissions centered at 540 nm and 658 nm are due to the transitions of Er^{3+}: $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$, respectively. On the other hand, the low phonon energy environment can also aid the rare earth up-conversion process. Therefore, after the CaF_2 nano-crystal is precipitated in the matrix, the up-conversion intensity is increased nearly ten times compared to that of the host glass sample (Fig. 4(b)). Besides, the quenching of the up-conversion luminescence is decreased to 3 mol% Yb^{3+} doping, which indicates that the high efficient up-conversion can be realized in the glass ceramics with less sensitizer Yb^{3+} ions. These results reveal that the influence of the microcrystal structure plays a crucial role to improve the efficiency of the Er^{3+} up-conversion. There are papers reporting that the size or morphology of the introduced nanoparticles can affect the luminescence properties of the emitters in materials.[1] In the following work, different heat treatment time is proceeded on the 0.5 mol% Er^{3+}–3 mol% Yb^{3+} co-doped glass in order to study the size influence on the up-conversion luminescence which is show in (Fig. 5).

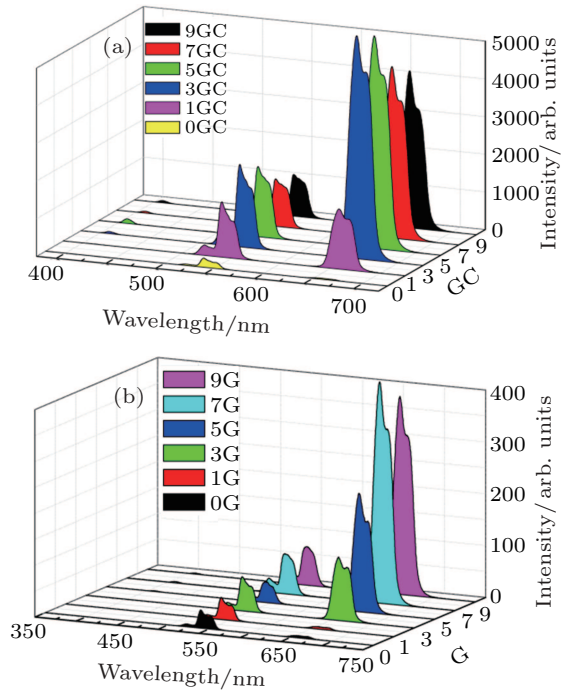


Fig. 4. (color online) (a) Visible up-conversion luminescence spectra of glass-ceramics with different Yb^{3+} contents under the excitation of 980 nm. (b) Visible up-conversion luminescence spectra of host glass with different Yb^{3+} contents under the excitation of 980 nm.

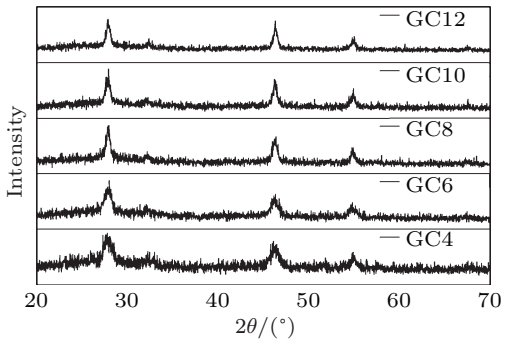


Fig. 5. XRD patterns of the heat treated glasses with different (from 4 h to 12 h) treatment times.

Obviously, the crystal size and the volume fraction of crystalline phase in the glass ceramics are increased with increasing the heat time at 680 °C, and the glass is still transparent until heat treated for 12 h. The crystallinity also becomes better in the long-time heat treated samples, which can be seen in Fig. 5, meaning the growth of the CaF_2 nano-crystal in the heat treatment process. The crystal size grows from 20.7 nm to 33.2 nm with the heat treatment time getting longer (the size is calculated by using Scherrer's equation). With the crystal size increased, the intensity of the up-conversion luminescence also changes, moreover, the red and the green

wavelengths present different ranges of increasing, which are shown in Fig. 6.

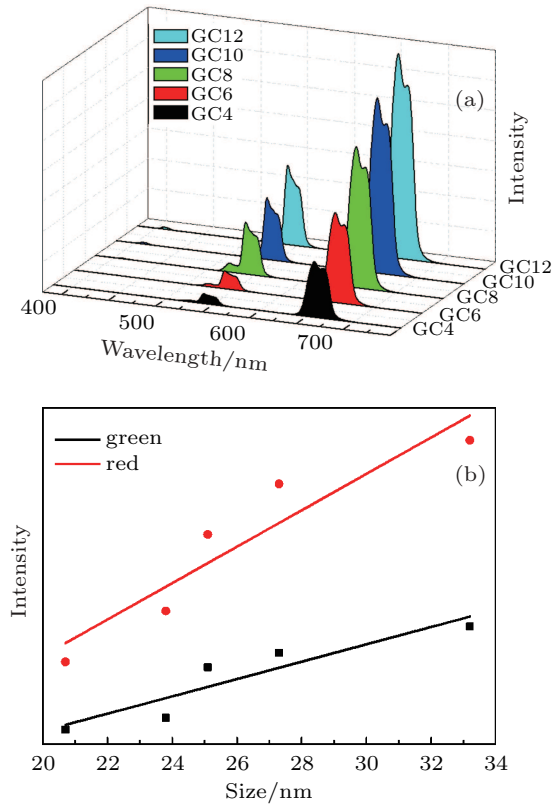


Fig. 6. (color online) (a) Visible up-conversion luminescence spectra of glass ceramics heated at 680 °C for different hours. (b) The up-conversion intensities at the red and the green wavelengths versus the nano-crystal size.

Figure 6(a) shows the up-conversion luminescence spectra of the glass ceramics heated at 680 °C for different hours. All the samples were measured under the same conditions and all the heat treated glasses were transparent. With the heat treatment time increasing, the up-conversion intensities at the red and the green wavelengths both increase significantly. This phenomenon may suggest that the longer the heat treatment time, the bigger size of the CaF_2 nano-crystal, and more rare earth ions are incorporated into the bigger CaF_2 nano-crystal, resulting in a high luminescent efficiency of the Er^{3+} up-conversion, similar results have been observed in the previous works.[1,24] Another notable phenomenon is that the luminescence enhancement of the red part is stronger than that of the green part with the size increase of the nano-crystal, which is shown in Fig. 6(b). This implies that different up-conversion mechanisms are responsible for the green and the red emissions of Er^{3+} in the glass ceramics.

To further illuminate this physical process, the mechanism of the up-conversion process is depicted in Fig. 7. As shown in Fig. 7, firstly, Yb^{3+} is excited from the ground state $^2F_{7/2}$ level to the excited state $^2F_{5/2}$ level under 980 nm pumping, and then transfers its energy to Er^{3+}. The electron on the Er^{3+}: $^4I_{15/2}$ ground state absorbs an excitation photon and is excited to the $^4I_{11/2}$ excited state (GSA), the electron at the $^4I_{11/2}$ excited state can be raised to the $^4F_{7/2}$ level by the excited state absorption (ESA) and then relaxes non-radiatively to $^2H_{11/2}$ and $^4S_{3/2}$ levels, and the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions take place, forming the green emissions of Er^{3+}. For the mechanism of the red emission, two possible pathways may exist. Firstly, the electrons on the $^4I_{11/2}$ state can relax to the $^4I_{13/2}$ level non-radiatively, with the energy transfer from Yb^{3+}, the electrons on the excited state are promoted to the higher excited state of the $^4F_{9/2}$ level, a red emission occurs when they come back to the ground state. On the other hand, the cross relaxation of $^4S_{3/2}+{}^4I_{9/2} \rightarrow {}^4F_{9/2}+{}^4I_{11/2}$ between two neighbor Er^{3+} ions can also realize the population of the Er^{3+}: $^4F_{9/2}$ excited state from which there is a red emission. In general, the green luminescence is dominated by the excited state absorption, while the red luminescence is dominated by the energy transfer. Since the efficiency of energy transfer between two ions is related to their distance, i.e., $\eta \propto 1/R^6$, therefore, with the heat treatment time getting longer, more rare earth ions are incorporated into the CaF_2 nano-crystals, the distance between the rare earth ions becomes shorter, leading to a high efficient energy transfer, which gives raise to the strong red emission. To sum up, the energy transition effect is more significant compared to the excited state absorption with increasing size of the precipitated nano-crystals, resulting in the more efficient red up-conversion luminescence. In this case, with increasing crystal size, more and more rare earth ions are concentrated in the nano-crystals and the emission intensity becomes stronger.[24]

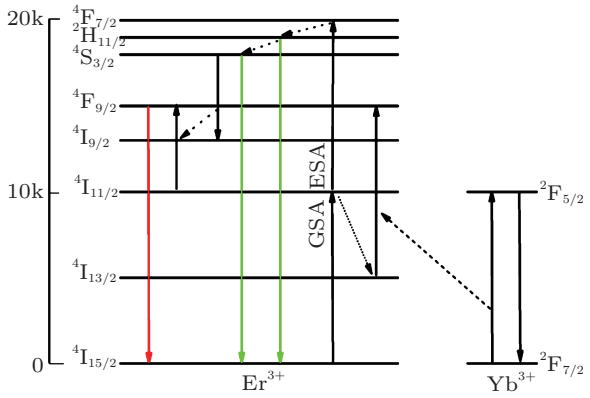


Fig. 7. (color online) Energy level diagram of Er^{3+} and Yb^{3+} ions, illustrating possible up-conversion pathways for the Er^{3+}/ Yb^{3+} co-doped glass ceramics.

4. Conclusion

Er^{3+}/Yb^{3+} co-doped transparent oxyfluoride glass ceramics containing CaF_2 nano-crystals were successfully prepared. Comparing with the sample without heat treatment,

a significant increase of the up-conversion luminescence was obtained in the heat treated sample. The concentration quenching point in this formula was decreased to 0.5 mol% Er^{3+}/3 mol% Yb^{3+}. Moreover, with increasing heat treated time, the size of the crystals became bigger and the up-conversion luminescence intensity of Er^{3+} could be further enhanced in the glass ceramics. The influence of the heat treatment on the red emission is more significant than that on the green emission. The phenomenon is caused by the shortened distance of rare earth ions and the enhanced energy transfer due to more rare earth ions incorporated into the CaF_2 nano-crystals, resulting in the more efficient energy transfer from Yb^{3+} to Er^{3+} in the CaF_2 nano-crystals. Therefore, the red up-conversion emission based on the energy transfer is more efficient than the green up-conversion emission based on the excited state absorption.

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