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Green and red up-conversion emissions and thermometric application of Er^{3+}-doped silicate glass*

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The green and red up-conversion emissions centred at about 534, 549 and 663 nm of wavelength, corresponding respectively to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+} ions, have been observed for the Er^{3+}-doped silicate glass excited by a 978 nm semiconductor laser beam. Excitation power dependent behaviour of the up-conversion emission intensity indicates that a two-photon absorption up-conversion process is responsible for the green and red up-conversion emissions. The temperature dependence of the green up-conversion emissions is also studied in a temperature range of 296–673 K, which shows that Er^{3+}-doped silicate glass can be used as a sensor in high-temperature measurement.

Keywords: Er^{3+}-doped silicate glass, up-conversion emission, fluorescence intensity ratio
PACC: 4270C, 3250F, 0720K

1. Introduction

In last decades, much attention has been paid to the short-wavelength emissions of rare-earth doped materials because of their many potential applications, such as colour display, high-density data reading and storage, biomedical diagnostics, and so on.[1−3] Of them, Er^{3+}-doped materials play the most important role in the near-infrared optical amplifiers and visible lasers.[4−6] Recently, the study on Er^{3+}-doped glasses with strong up-conversion emissions has been extensively reported, for example, fluoride (halide) phosphate tellurite glass,[7] bismuth-borate glass[8] and oxyfluoride glass.[9] Thermal effect on up-conversion fluorescence emission of Er^{3+}-doped chalcogenide glasses[10] and Er^{3+}-doped Li:TeO_2 glasses[11] was investigated. Some Er^{3+}-doped glasses were also found to be sensitive temperature sensors.[12−14] The above-mentioned Er^{3+}-doped glass materials can operate only at temperatures below 530 K due to lower chemical durability and thermal stability. Er^{3+}-doped silicate glass, however, possesses better qualities, fluorescence efficiency and longer decay time.[15,16] In this paper, Er^{3+}-doped silicate glass is prepared. The green and red up-conversion emissions are measured and photoluminescence mechanism is also presented. The 534 and 549 nm spectral lines in a temperature range of 296–673 K are observed easily with a few tens of milliwatts of pump power. The fluorescence intensity ratio (FIR) of spectral lines at 534 and 549 nm of wavelength can be used for sensitive high-temperature measurement.

2. Experiment

The original compositions composed of the 0.8at.% Er^{3+}-doped silicate glass include Er_2O_3 (9.41 g), SiO_2 (66.35 g), $BaCO_3$ (10.75 g), $B(OH)_3$ (3.07 g) and Na_2O_3 (10.42 g). Their mixed powder was homogenized, compacted, and heated at 1723 K for 30 min in a high-temperature furnace. When the Er^{3+}-doped glass stock was in a molten state, it was poured into two moulds and moved into another furnace at 873 K. Ten minutes later they were taken out of the moulds, put on an asbestos web, and maintained for three hours. Then the Er^{3+}-doped silicate glasses cooled down to room temperature naturally in the second furnace. Finally, they were incised into

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pieces each with a dimension of 20 mm×10 mm×2 mm and then polished.

The Er^{3+}-doped silicate glass was placed in the front of a heater where the temperature could change from 296 to 673 K within a measurement error of ±1.5 K. The green and red up-conversion emission spectra in a wavelength range of 500–750 nm were obtained from the sample excited by a 978 nm semiconductor laser beam. The working current of the laser varied from 0 to 2000 mA, and the corresponding pump power in a ∼4 mm diameter spot went up to 1 W. The emission from the Er^{3+}-doped silicate glass was focused onto a monochromator, and detected with a CR131 photomultiplier tube equipped with a lock-in amplifier. The spectral resolution of the experimental set-up was 0.1 nm.

3. Results and discussion

Figure 1 shows the room-temperature up-conversion emission spectra of the Er^{3+}-doped silicate glass in a wavelength range of 500–750 nm. The spectra centred at about 534, 549 and 663 nm are attributed to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions of trivalent erbium ions, respectively. The numerous Er^{3+} ions distribute randomly in the substrate of silicate glass and face various environments, leading to the inhomogeneous broadening of the up-conversion emission peaks. So we cannot observe the Stark splitting in Fig.1.

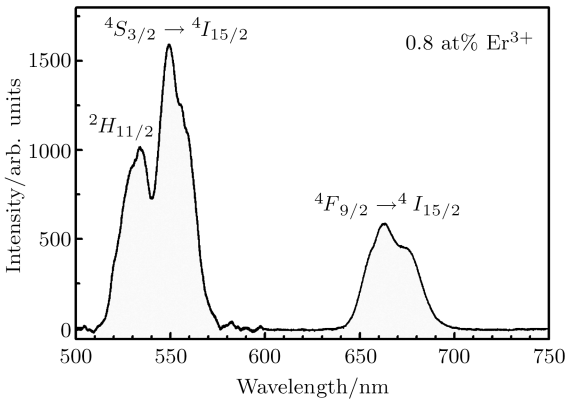


Fig.1. Up-conversion emission spectra of the Er^{3+}-doped silicate glass measured at room-temperature

Figure 2 gives the logarithmic dependence of peak intensity of green and red up-conversion emissions centred at about 534, 549, and 663 nm as a function of pump power. For our Er^{3+}-doped silicate glass, the up-conversion emission intensity (I_{up}) is proportional to the nth power of pump power (P_{pump})[17,18] as expressed below:

$$I_{up} \propto P_{pump}^{n}, \tag{1}$$

where n is the number of photons required to populate the green and red up-conversion emission states. The experimental data of up-conversion emission intensity are fitted to straight lines with a slope of n. The values of n are approximately in a range of 1.42–1.66 for the green and red up-conversion emissions centred at about 534, 549, and 663 nm, indicating that the two-photon process is involved in the green and red up-conversion emission mechanism for the Er^{3+} doped silicate glass. Based on the energy matching conditions and quadratic dependence on pump power, it is proposed that the excited state absorption (ESA) and cross-relaxation (CR) processes are responsible for the green and red up-conversion emissions of the Er^{3+}-doped silicate glass.

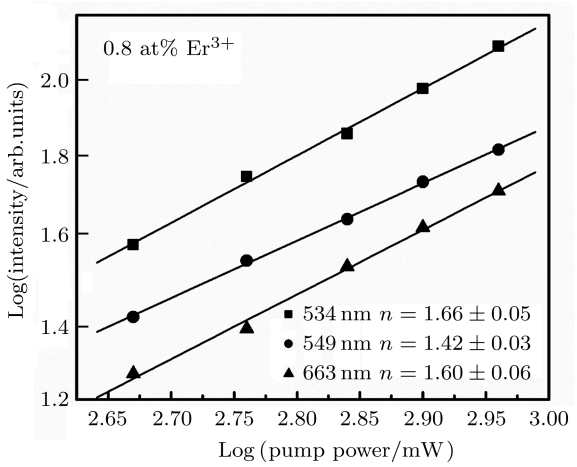


Fig.2. Logarithmic dependence of peak intensity of the green and red up-conversion emissions as a function of the pump power.

Figure 3 is the energy level diagram of the green and red up-conversion emissions for the Er^{3+}-doped silicate glass excited by a 978 nm semiconductor laser (LD) beam. The green and red up-conversion emissions originate from the transitions of $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ of Er^{3+} ion levels. In the Er^{3+}-doped silicate glasses, the dominant mechanisms responsible for the green and red emissions of Er^{3+} ions are the ESA and CR. For the red up-conversion emission, the population of the $^4F_{9/2}$ level is ascribed to the combined process of the multiphoton relaxation from the $^4S_{3/2}$ level, the ESA ($^4I_{13/2}$+a photon$\rightarrow {}^4F_{9/2}$), and the CR (II, III, IV)

$\left({}^4I_{9/2} + {}^4I_{11/2} \rightarrow {}^4I_{13/2} + {}^4F_{9/2},\ {}^4I_{11/2} + {}^4I_{13/2} \rightarrow {}^4I_{15/2} + {}^4F_{9/2}\right.$ and $\left.{}^4F_{7/2} + {}^4I_{11/2} \rightarrow {}^4F_{9/2} + {}^4F_{9/2}\right)$. But for two green up-conversion emissions, the populations of the $^2H_{11/2}$ and $^4S_{3/2}$ levels are mostly from the $^4F_{7/2}$ level by nonradiative decay. From Fig.3, we can also see that the $^4F_{7/2}$ level is populated by the ESA ($^4I_{11/2}$+a photon$\rightarrow$ $^4F_{7/2}$) and the CR(I) ($^4I_{11/2}$+$^4I_{11/2} \rightarrow {}^4I_{15/2}$+$^4F_{7/2}$) processes. Under the energy unmatching condition, the silicate glass matrix with a maximum phonon energy of 1000 cm^{-1} can facilitate the realization of CR processes by phonon-assisted energy transfer. The processes are greatly dependent on the phonon energy of matrix.

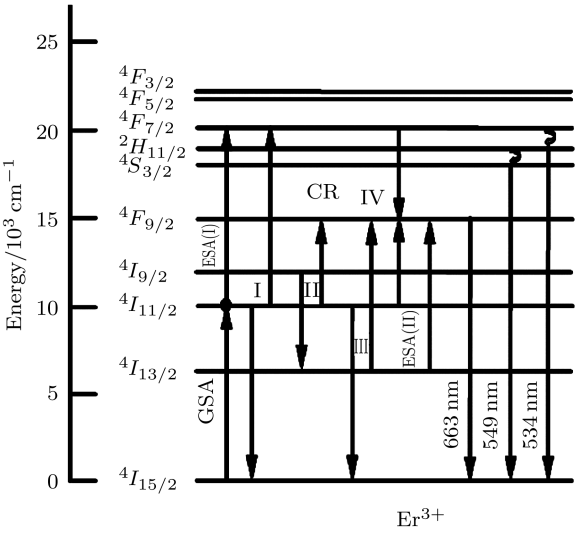


Fig.3. Energy level diagram of the green and red up-conversion emissions from the Er^{3+}-doped silicate glass excited by a 978 nm laser beam.

Moreover, the $^2H_{11/2}$ level may be also populated from the $^4S_{3/2}$ level by thermal excitation due to a small energy gap between the two levels, with a value of about 512 cm^{-1} estimated from the green up-conversion emission spectra. It is well known that the relative population between $^2H_{11/2}$ and $^4S_{3/2}$ levels follows a Boltzmann-type population distribution, i.e. a quasiequilibrium exists.[19,20] When the temperature is elevated, the population of $^4S_{3/2}$ level transfers into $^2H_{11/2}$ level because of thermally coupling, which results in the variation of the transition intensities of $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ of Er^{3+} ions. The fluorescence intensity ratio (FIR) of green up-conversion emissions at about 534 nm and 549 nm can be written as

$$\mathrm{FIR} \equiv \frac{I_{534}}{I_{549}} = \frac{N(^2H_{11/2})}{N(^4S_{13/2})} = \frac{g_\mathrm{H}\sigma_\mathrm{H}\omega_\mathrm{H}}{g_\mathrm{S}\sigma_\mathrm{S}\omega_\mathrm{S}} \exp\left[\frac{-\Delta E}{kT}\right] = C\exp\left[\frac{-\Delta E}{kT}\right], \quad (2)$$

where N, g, σ, ω_S and ω_H are the population density of ions, the degeneracy, the emission cross-section and the angular frequencies of fluorescence transitions from the $^2H_{11/2}$, $^4S_{3/2}$ levels to $^4I_{15/2}$ level, ΔE is the energy gap between the $^2H_{11/2}$ and $^4S_{3/2}$ levels, k the Boltzmann constant, T the absolute temperature and the constant $C = g_\mathrm{H}\sigma_\mathrm{H}\omega_\mathrm{H}/(g_\mathrm{S}\sigma_\mathrm{S}\omega_\mathrm{S})$.

Figure 4 shows the green up-conversion emission spectra in a wavelength range of 500–600 nm for the Er^{3+}-doped silicate glass in a temperature range of 296–673 K. As shown in Fig.4, the two green up-conversion emission bands at about 534 nm and 549 nm remain almost the same, whereas the fluorescence intensity ratio of the two emissions increases with temperature elevating.

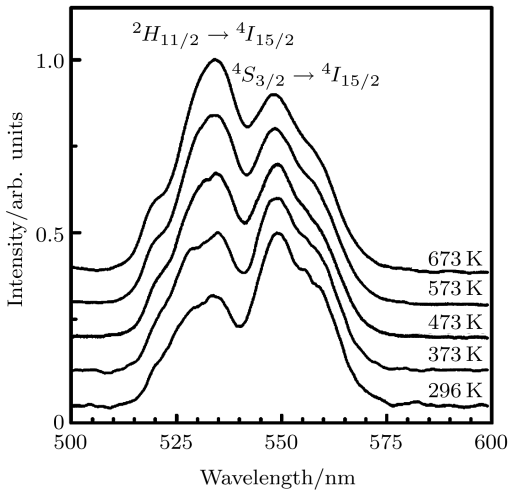


Fig.4. Green up-conversion emission spectra of the Er^{3+}-doped silicate glass in a temperature range of 296–673 K.

Table 1 gives a comparison between the temperature calculated by FIR technique (T_Cal) and the one measured by thermocouple (T_Mea) for different temperatures of the sample of Er^{3+}-doped silicate glass. It is shown that they are in reasonable agreement with each other in a temperature range of 296–673 K.

Thermal characteristics of Er^{3+}-doped chalcogenide glass and Er^{3+}-doped Li:TeO_2 glass were discussed in a temperature range of 300–473 K.[10,11] Er^{3+}-doped SiO_2 glass,[12] Er^{3+}-doped Li:TeO_2 glass,[13] Er^{3+}-doped Bi_2O_3–Li_2O–BaO–PbO tertiary glass[14] were reported to be sensitive temperature sensors and their upper-limit temperatures were 473, 530

and 428 K, respectively. Compared with them, our samples of Er^{3+}-doped silicate glass have an operating temperature extended up to 673 K, indicating that Er^{3+}-doped silicate glass has promising applications in high temperature measurement.

Table 1. A comparison between temperatures calculated by FIR technique and measured by thermocouple.

FIR(I_{534}/I_{549})	T_{Cal}/K	T_{Mea}/K	ΔT/K
0.640	295.8	296	0.2
0.812	372.7	373	0.3
0.987	472.5	473	0.5
1.098	573.4	573	0.4
1.174	673.7	673	0.7

4. Conclusions

In this work, we have prepared samples of Er^{3+}-doped silicate glass, discussed the up-conversion emission mechanism, and proved that the two-photon absorption process is involved in the up-conversion mechanism for the green and red up-conversion emissions. We also have measured temperature-dependent green up-conversion emission spectra in a range of 296–673 K and proved that the ESA and CR processes are responsible for the green and red up-conversion emissions. The optical material can be applied to sensitive temperature measurement based on the fluorescence intensity ratio (FIR) of 534 and 549 nm spectral lines. The measurable upper-limit temperature is extended up to 673 K, excelling other Er-doped materials reported. Yb:Er co-doped alumina materials will be an important object in our next work, because they can improve photoluminescence intensity remarkably, and they are possessed of more outstanding temperature properties.

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