Sensors **2007**, *7*, 2652-2659

sensors

ISSN 1424-8220

www.mdpi.org/sensors

Full Research Paper

Application to Temperature Sensor Based on Green Up-Conversion of Er^{3+} Doped Silicate Glass

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Received: 7 September 2007 / Accepted: 22 October 2007 / Published: 8 November 2007

Abstract: The green up-conversion emissions centered at the wavelengths of about 534nm and 549nm of the Er^{3+} doped silicate glass were recorded, using a 978 nm semiconductor laser diode (LD) as an excitation source. The fluorescence intensity ratio (FIR) of the green up-conversion emissions at about 534nm and 549nm in the Er^{3+} doped silicate glass was studied as a function of temperature over the temperature range of 296K-673K. The maximum sensitivity and the temperature resolution derived from the FIR of the green up-conversion emissions are approximately $0.0023K^{-1}$ and 0.8K, respectively. It is demonstrated that the prototype optical temperature sensor based on the FIR technique from the green up-conversion emissions in the Er^{3+} doped silicate glass could play a major role in temperature measurement.

Keywords: Er^{3+} doped silicate glass; Optical temperature sensor; Green up-conversion emissions; Fluorescence intensity ratio

PACS classification codes: 78.55.Hx; 81.40.Tv

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1. Introduction

Infrared to visible up-conversion emissions in rare-earth doped glass materials have received significant attention due to a wide range of applications such as short-wavelength laser, infrared viewers and indicators, sensors, color displays, high density optical data reading and storage, etc. [1-7]. Among the rare-earth ions, Er^{3+} is the most popular as well as one of most efficient ions because it has a favorable energy level structure with $^4I_{15/2} \rightarrow {}^4I_{11/2}$ transition in the near-infrared spectral region which can be easily excited using a 978nm semiconductor laser as excitation source [3-7]. Recently, a number of optical temperature sensors have been presented and the most outstanding approach is based on the fluorescence intensity ratio (FIR) technique [8-12], which can help to reduce the influence of measurement condition and therefore, improve the measurement sensitivity. Some previous works about optical temperature sensors using the FIR technique from green up-conversion emissions of Er^{3+} are mainly focused on fluoroindate glasses and chalcogenide glasses [11,12], however, which can operate only at temperatures below 523K because lower chemical durability and thermal stability. Compared with the other glasses, Er^{3+} doped silicate glass possesses higher chemical durability and thermal stability and it could be more easily fabricated into different products for use, such as Er^{3+} doped fiber optical sensor for temperature measurement because of perfect match of the compositions between fiber and our silicate sample. Moreover, extensive research of the photoluminescence (PL) properties of Er^{3+} doped silicate glass proved that silicate glass is more appropriate as the Er^{3+} doped matrix for it possesses improved fluorescence efficiency and decay time [13,14].

In this paper, we present experimental results of green up-conversion emissions of Er^{3+} doped silicate glass in the temperature range of 296K-673K, in order to explore a developing possibility of optical high temperature sensor based on the FIR technique from the green up-conversion emissions.

2. Experimental

The 100.000g powders with corresponding compositions of $9.41Er_2O_3$-$66.35SiO_2$- $10.75B_2O_3$-$3.07BaO$-$10.42Na_2CO_3$ (g) were homogenized and compacted in 50ml corundum crucible, then heated at 1723K for 30min in the high-temperature furnace. When the glass stock of Er^{3+} doped took on molten state, it was poured into moulds and then moved into another furnace at 873K. After 10min, the samples were taken out of the moulds, put on asbestos web and maintained for 3h, then cooled down to room temperature naturally in the furnace. The 0.8at% Er^{3+} doped silicate glass samples were incised with dimension of 10mm×10mm×3mm and polished.

The sample was placed in a furnace and its temperature from 296K to 673K with measurement error of $\pm$1.5K was monitored with a copper-constantan thermocouple set to its back-face. The green up-conversion emissions spectra in the wavelength range of 500nm- 600nm were detected from the sample using a 978nm semiconductor laser diode (LD) as an excitation source with excitation power of 0.8W, corresponding to a power density of 4.0×10^2 W cm^{-2}. The green up-conversion emissions were focused onto a single-monochromator, and detected with a CR131 photomultiplier tube associated with a lock-in amplifier. The spectral resolution of the experimental set-up was 0.1nm.

3. Results and Discussion

Figure 1 shows a simplified energy level diagram of the green up-conversion emissions for the Er^{3+} doped silicate glass by a 978 nm LD excitation [15,16]. The excited state absorption (ESA) of $^4I_{11/2}$+a photon→$^4F_{7/2}$ and cross-relaxation (CR) of $^4I_{11/2}$+$^4I_{11/2}$→$^4I_{15/2}$+$^4F_{7/2}$ populate the Er^{3+} on $^4F_{7/2}$ level by following the ground state absorption (GSA) of $^4I_{15/2}$+a photon→$^4I_{11/2}$, and a nonradiative decay from $^4F_{7/2}$ to $^2H_{11/2}$ and $^4S_{3/2}$ levels produce the final green up-conversion emissions population of Er^{3+}. The transitions of $^2H_{11/2}$→$^4I_{15/2}$ and $^4S_{3/2}$→$^4I_{15/2}$ are responsible for the green up-conversions emissions at about 534nm and 549nm, respectively.

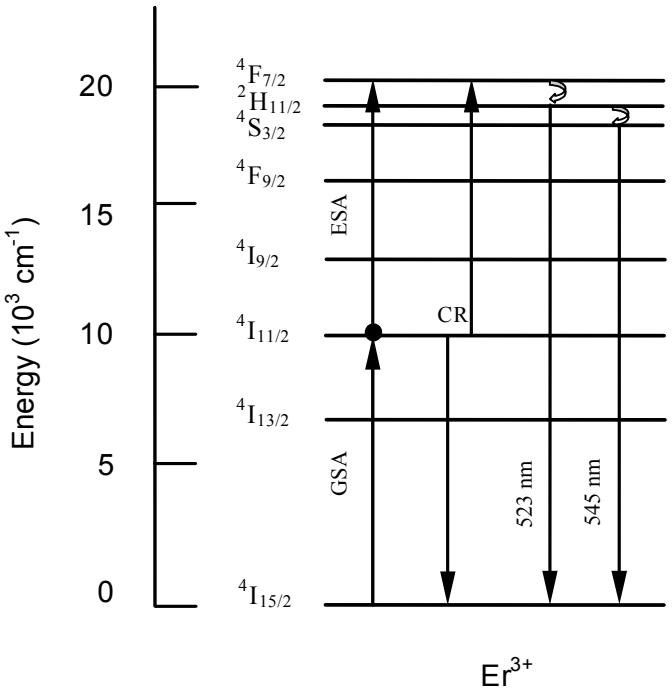

Figure 1. The energy level diagram of the green up-conversion emissions for the Er^{3+} doped silicate glass by a 978 nm laser excitation.

Figure 2 shows the green up-conversion emissions spectra in the wavelength range of 500nm-600nm for the Er^{3+} doped silicate glass at the measured temperature of 296K and 633K. The two green up-conversion emissions bands at about 534nm and 549 nm correspond to the $^2H_{11/2}$→$^4I_{15/2}$ and $^4S_{3/2}$→$^4I_{15/2}$ transitions of Er^{3+}, respectively. The two bands positions of green up-conversion emissions show no change with increasing temperature, whereas the FIR of the two emissions varies. 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 512cm^{-1} as estimated from the green up-conversion emissions spectra. The relative population of the "thermally coupled" $^2H_{11/2}$ and $^4S_{3/2}$ levels follows a Boltzmann-type population distribution, i.e. a quasiequilibrium exists [9,12], leading to variation in the transitions of $^2H_{11/2}$→$^4I_{15/2}$ and $^4S_{3/2}$→$^4I_{15/2}$ of Er^{3+} at the elevated temperature. With thermalization of populations at the $^2H_{11/2}$ and $^4S_{3/2}$ levels, the FIR of green up-conversion emissions at about 534nm and 549nm can be written as

$$R \equiv \frac{I_{534}}{I_{549}} = \frac{N(^2\mathrm{H}_{11/2})}{N(^4\mathrm{S}_{3/2})} = \frac{g_H \sigma_H \omega_H}{g_S \sigma_S \omega_S} \exp\left[\frac{-\Delta E}{kT}\right] = C \exp\left[\frac{-\Delta E}{kT}\right] \quad (1)$$

where N, g, σ, ω, are the number of ions, the degeneracy, the emission cross-section, the angular frequency of fluorescence transitions from the $^2H_{11/2}$, $^4S_{3/2}$ levels to $^4I_{15/2}$ level, ΔE the energy gap between the $^2H_{11/2}$ and $^4S_{3/2}$ levels, k the Boltzmann constant, T the absolute temperature, the preexponential constant is given by $C = g_H\sigma_H\omega_H / g_S\sigma_S\omega_S$.

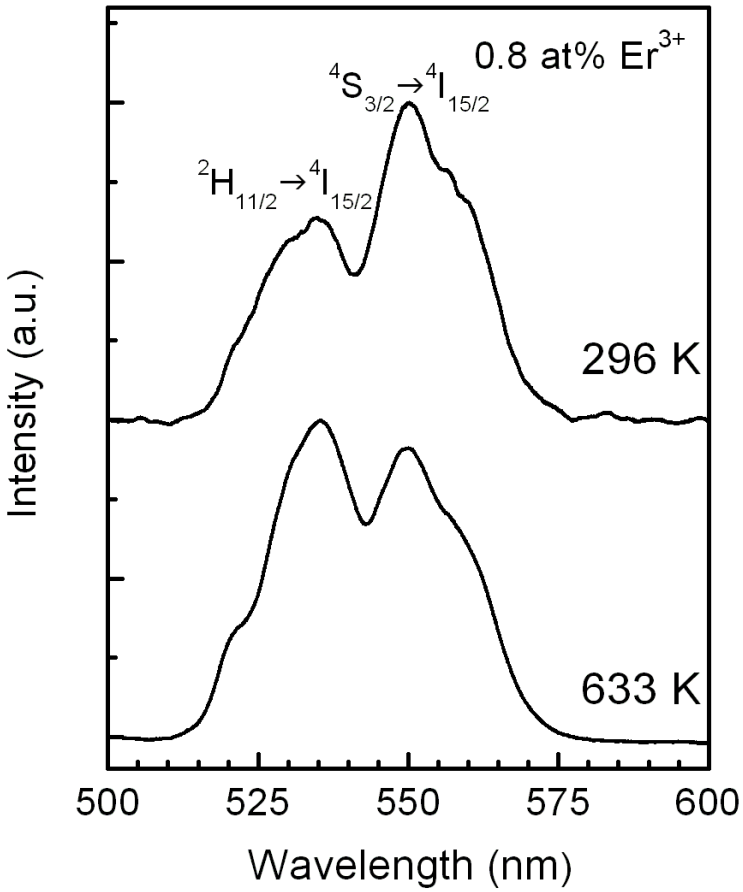

Figure 2. The green up-conversion emissions spectra in the wavelength range of 500nm-600nm for the Er^{3+} doped silicate glass at the measured temperature of 296K and 633K.

Figure 3 shows a monolog plot of the FIR of green up-conversion emissions at about 534nm and 549nm as a function of inverse absolute temperature in the range of 296K-673K. The experimental data could be fitted by straight line with a slope of about 335. The FIR of green up-conversion emissions at about 534nm and 549nm relative to the temperature range of 296K-673K is shown in Figure 4. The FIR increases from about 0.60 to 1.14 from 296K to 673K. The value of coefficient C in the Equation (1) is 1.87 according to the linear fit of the experimental data. The sensor sensitivity can be defined as:

$$\frac{dR}{dT} = R\left(-\frac{\Delta E}{kT^2}\right) \quad (2)$$

and a curve of sensitivity against T is shown in Figure 5. At a temperature of 296K, the sensitivity of Er^{3+} doped silicate glass reached its maximum value of about $0.0023K^{-1}$, and its minimum value of about $0.0008K^{-1}$ at 673K.

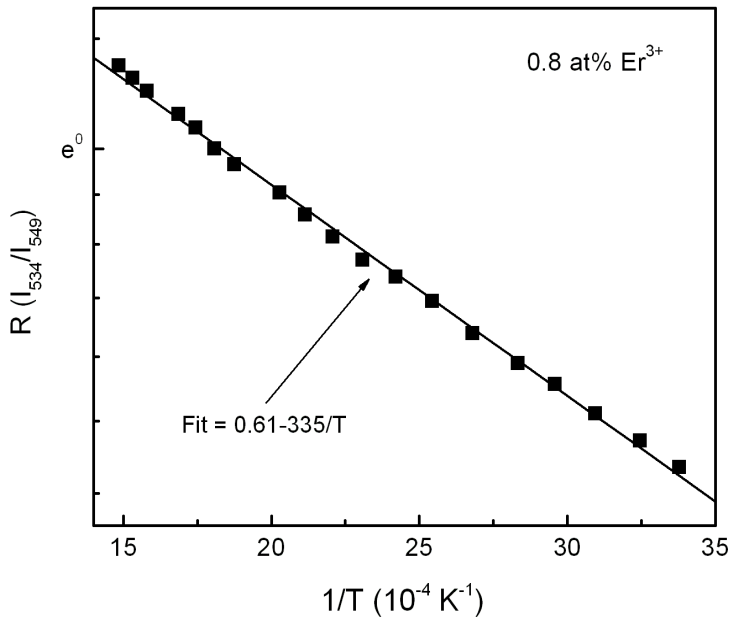

Figure 3. The monolog plot of the FIR of green up-conversion emissions at about 534nm and 549 nm as a function of inverse absolute temperature in the range of 296K-673K.

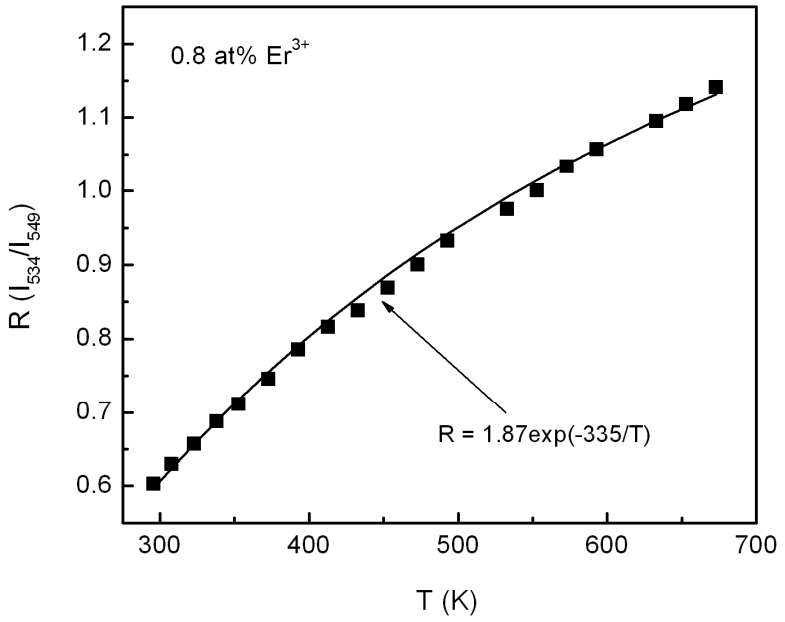

Figure 4. The FIR of green up-conversion emissions at about 534nm and 549nm relative to the temperature range of 296K-673K.

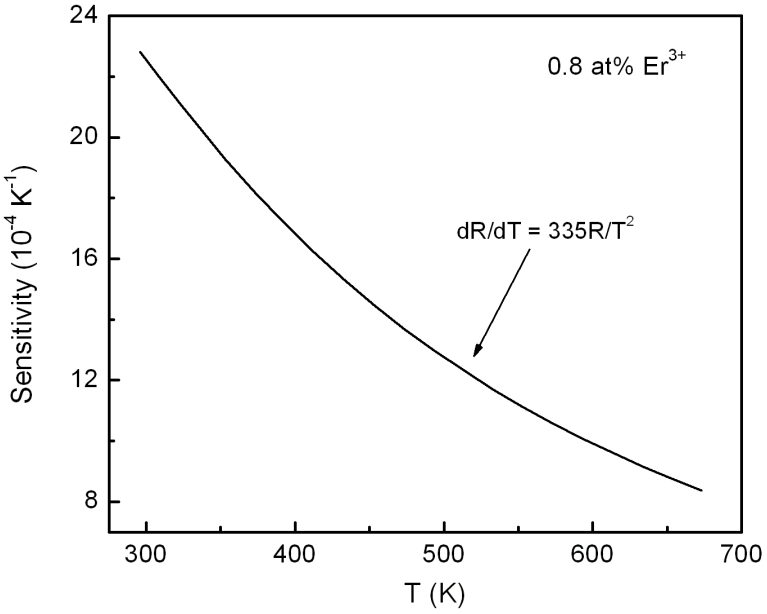

Figure 5. The sensor sensitivity *dR/dT* as a function of the temperature range of 296K-673K.

In the temperature range of 296K-673K, the optical temperature sensors based on Er^{3+} doped silicate glass achieved a favorable result. Here, the operating temperature of 673K and sensitivity of $0.0023K^{-1}$, which excelled 448K and $0.004K^{-1}$ in fluoroindate glass [11], and 523K and $0.0052K^{-1}$ in chalcogendie glass [12], respectively. From Equation (2), the sensitivity depends on the ΔE. Thus, the Er^{3+} doped silicate glass possesses a better sensitivity because its ΔE of $512cm^{-1}$ is smaller than that of fluoroindate glass ($\Delta E \approx 742cm^{-1}$) and chalcogendie glass ($\Delta E \approx 850cm^{-1}$). The temperature resolution for the Er^{3+} doped silicate glass was also relatively high, at about 0.8K by employing a signal division circuitry with a precision of four digits or more. Another important aspect to consider is the suitability of the Er^{3+} doped silicate glass to be fibered, and the possibility to the use the doped fiber as the active sensing element. Finally, a prototype optical high temperature sensor based on the FIR technique of the green up-conversion emissions in the Er^{3+} doped silicate glass appears promising for applications in high temperature measurement.

It is worthwhile to point out that the Er^{3+} doped silicate glasses with different dopant concentrations (0.1, 0.2, 0.4, 0.6 and 0.8at%) were prepared and investigated based on the FIR technique under different temperature. All samples showed the similar high temperature sensing properties. Compared with other samples, 0.8at% Er^{3+}-doped silicate glass has the strongest green up-conversion emissions and can be detected with lower pumping power, indicating that it is more in favor of application in temperature measurement.

4. Conclusions

The green up-conversion emissions at about 534nm and 549nm which from the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+}, respectively, were detected in the temperature range of 296K-673K for the Er^{3+} doped silicate glass. The two bands positions of green up-conversion emissions have no change with the higher temperature of Er^{3+} doped silicate glass. With increasing the measured

temperature from 296K to 673K for the Er^{3+} doped silicate glass, the FIR of green up-conversion emissions at about 534nm and 549nm increased linearly due to populating the $^2H_{11/2}$ level was populated from the $^4S_{3/2}$ level by thermal excitation and quasithermal equilibrium processes in the two levels. For the optical high temperature sensor based on the FIR technique of the green up-conversion emissions in the Er^{3+} doped silicate glass, the maximum sensitivity and the temperature resolution are approximately $0.0023K^{-1}$ and 0.8K in the temperature range of 296K-673K, respectively.

Acknowledgements

We acknowledge the technical assistance of Songqiang Zhou in this research. This work is supported by the Science and Technology Commission of Liaoning Province (Grant No.20062137).

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