Micrometer-sized point temperature sensor in Er:ZBLALiP

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ABSTRACT

A new kind of Erbium-doped heavy fluoride glass Er:ZBLALiP was elaborated, and microspheres were fabricated with this fluoride glass. Thermal properties and spectroscopic properties of Er:ZBLALiP excited at 805 nm were investigated. Based on this thermalization effects between upper levels of green fluorescence in Er:ZBLALiP, we proposed an optical temperature sensing using micrometer-sized spherical cavity. The sphere temperature is scaled by the ratio of green emission intensities at 522 and 547 *nm*. A wide dynamic temperature ranging from 100 K to 850 K can be utilized by this type of point temperature sensor.

Keywords: Er:ZBLALiP, Point sensor, Modeling, Green emission, Diode-pumping

1. INTRODUCTION

The heavy-metal fluoride glass doped with rare-earth ions becomes attractive both in materials and in laser–matter interaction[1]. The most attractive among them is Erbium-doped glasses, which are extremely investigated since last decade. Several groups have reported the thermal properties as well as the spectroscopic behaviors on Erbium-doped bulkglasses[2-5] and optical fibers[6-7]. In these literatures, optical temperature sensing using green upconversion fluorescence emission in Er^{3+}- or Er^{3+}/Yb^{3+}-codoped glasses have been investigated. By compared with Erbium-doped bulk glass or optical fiber sensors, point sensor possess several advantages in techniques and applications. Firstly, Erbium-doped glass microspheres are easy to fabricate with great quantity resulting in very low cost per sensor. Secondly, intense green upconversion emission from diode-pumped Erbium-doped fluoride microspheres makes the measurement hardware rather simple and reliable. Finally, microsphere point temperature sensor, with combining an active dimension ranging from ten to hundred micrometers in diameter and large dynamic temperature sensing, allows it very suitable in specific applications when micrometer spatial resolution is needed.

A new kind of Erbium-doped heavy-metal fluoride glass, Er:ZBLALiP, was elaborated for the first time and microspheres were fabricated by microwave plasma torch. An initial experimental study on thermal properties and spectroscopic properties of Er:ZBLALiP microsphere excited by an 805nm laser diode(LD) was presented in this paper. Based on this thermalization effects between upper levels of green fluorescence in Er:ZBLALiP, we propose a new optical temperature sensor using micrometer-sized spherical cavity composed of Erbium-doped fluoride glass.

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2. EXPERIMENTAL INVESTIGATION

The fluoride glass elaboration and microsphere fabrication are firstly outlined, then the spectroscopic properties of Er:ZBLALiP are experimentally investigated.

2.1 Microsphere fabrication

A new kind of lead fluoride glass, Er:ZBLALiP, is prepared in CNRS at Meudon, France. The composition of Er:ZBLALiP glass is $62.2ZrF_4,19.5BaF_2,6.1LaF_3,3.6AlF_3,2.4LiF,6.1PbF_2 +xErF_3$, where x is the Erbium doped concentration in percentage. Several concentration ranging from x=0.01% to 6% were prepared, corresponding approximately to 0.02 to 12×10^{20} *Er ions/cm*^{3}. Glass samples were melted in a covered platinum crucible at about 800°C for 45 min for melting and at 850°C for fining. Both treatments were performed in a dry chamber under argon atmosphere. The melt liquid was poured on a preheated copper mold at 260°C and slowly cooled down to room temperature. The resulting glassy sample was 3 mm thick. The melting point is 600°C for Er:ZBLALiP.

The microsphere is fabricated by microwave plasma flame. The bulk sample of Er:ZBLALiP is ground to fine powder and then is dropped through the microwave torch where it is heated and subsequently cooled in free fall. By changing the microwave power and argon-oxygen flux, the temperature of the microwave plasma flame can be varied from 800 to 2100°C which covers most laser glass and crystal melting point. High quality microspheres with diameter ranging from ten to hundred micrometers are easy to be obtained by controlling microwave plasma power along with the powder size. A 6% Er:ZBLALiP microsphere with 90 μm diameter was used in our experimental investigation.

2.2 Spectroscopic experiments

This microsphere is first glued onto one end of a piece of fiber tip with a diameter approximately equal to 40 μm, then supported on a thin aluminum chip for easy manipulation. The microsphere is directly excited by focusing an 805 nm LD through an objective, and the emission is collected through an identical objective then sent to an optical spectrum analyzer.

In order to investigate the evolution of emission spectra on the microsphere cavity temperature or on the incident pumping power, a LD with a maximum output power of 1 W was chosen as pumping source to measure green upconversion emission. Such a pumping source choose is due to the following considerations: (1). 1 W output power is enough intense to create large microsphere cavity temperature increase; (2). 805 nm is near the optimal pumping wavelength for Er:ZBLALiP to detect the green upconversion emission. It is shown in Fig.1-3 that a comparison of the emission spectra of Er:ZBLALiP under 805 nm and 1470 nm excitations, the pumping power is almost same and of order of a few of 10 mW for both excitations. It is clear that when excited at 1470 nm the strongest emission centered at 980 nm which is five times of the green emission centered at 547 nm and ten times of emission centered around 660 nm and 1530 nm. In this case the green upconversion is associated with three-photon excitation, while 980 nm emission with two-photon excitation. Under 805 nm excitation, the green unconversion emission intensity is comparable to that around 980 nm emission. In this case the green emission is associated with two-photon excitation while 980 nm emission with linear excitation, and green emission intensity grows relatively more fast than 980 nm emission intensity. It should be noted that a 980 nm LD is also suitable to be pumping source to detect green upconversion, and the performance is similar to 805 nm LD. But a high power LD at 980 nm is less widely commercialized.

The green emission spectra under 10 mW and 450 mW pumping levels are shown in Fig.2-3. We can see apparently that such green emission spectra consist of two peaks: the first one is centered at 522 nm and the other at 546 nm. Both peak wavelengths are shorter than that of Erbium-doped phosphate glass[2] or fluozirconate glass ZBLAN, and this blue-shift effect might be believed as the result of heavy fluoride glass ZBLALiP resulting in smaller Stark splitting in the groundstate of Erbium ions. Each emission spectra in Fig.2-3 can be decomposed into five Gaussian profiles by a

Multi-Gaussian-Fit procedure. The peak wavelengths of these five Gaussian profiles remain quasi-independent of the incident pumping power, being 518.7 nm, 522.0 nm, 527.4 nm, 541.6 nm and 550.4 nm, respectively, while their height and area are different as the pumping power is increased. It should be noted that under low-level pumping power, *i.e.*, 10 mW, the peak of 518.7 nm is very much weaker than others, while under high-level pumping power of 450 mW, the peak of 518.7 nm is grown to a comparable intensity to the other fours. Such behavior is believed to be due to the fact that the microsphere temperature rises as the pumping power increased, and this leads to enhance Erbium population on the higher Stark's manifold of the upper level responsible for the 522 nm transition. As observed in other host glasses[2-7], the emission intensities of these two green peaks are sensitive to the pumping power. From Fig.2-3, the evolution of green emission on the pumping power indicates a significant increase of the integrated intensity ratio of 522 nm over 546 nm bands from 0.23 to 0.72 between 10 mW and 450 mW pumping. To better clarify the originality of this effect, the emission spectra around 976 nm is also measured, as presented in Fig.4. Unlike the evolution of green emission on

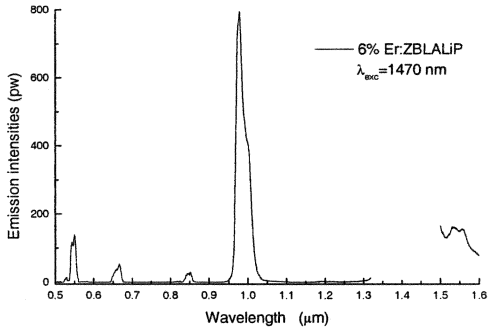

Fig.1 Upconversion emission spectrum of an Er:ZBLALiP when pumped at 1470 nm with 120 mw incident power.

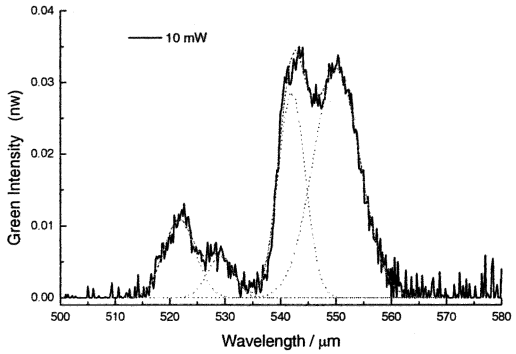

Fig.2 Green upconversion emission spectrum of an Er:ZBLALiP microsphere when pumped at 805 nm with 10 mw incident power.

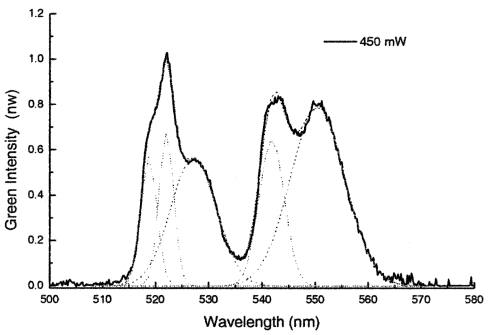

Fig.3 The same as Fig.2 but with 450 mw incident power.

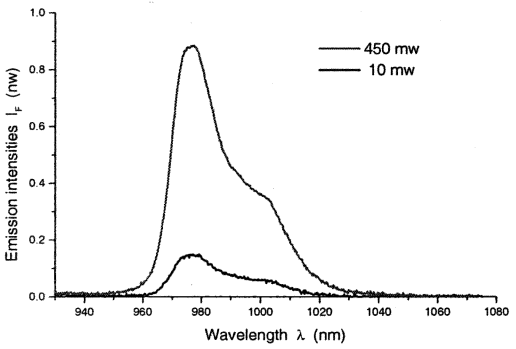

Fig.4 Evolution of emission spectra centered at 976 nm as the incident pumping power increased from 10 mW to 450 mW.

the pumping power as shown in Fig.2-3, although the emission spectra grow with pumping power increased the spectral profiles keep unchanged. The same behavior was observed for 1533 nm emission. This suggests that the green

upconversion emission depends strongly on the phonon-associated transition. Another interesting behavior is that the green emission intensity is much weaker than that around 976 nm under lower pumping, while the former emission becomes stronger than the latter one under high pumping, as in Fig.2, Fig.3 and Fig.4.

3. TEMPERATURE MODELLING

Fig.5 represents energy-level diagram of Erbium-doped ZBLALiP with 805 nm laser excitation. Evidently, from the green emission spectra in Fig.2-3, these five decomposed profiles(the former two and the later three ones) belong to two green emissions which are attributed to the transitions from the $^2H_{11/2}$(level 3), and $^4S_{3/2}$(level 2) metastable levels to the $^4I_{15/2}$ fundamental level(level 1) of the Erbium ions. The central wavelengths of these two bands are 522 nm and 546 nm, which are calculated by weighting the Stoke's shifts, and their FWHMs are 15 nm and 18 nm, respectively. The excitation mechanism on Erbium ions have been extensively described by several authors[2-8], and here do not repeat it but some key properties about Er:ZBLALiP is briefly given to understand better the experimental results. Excitation process for the green upconversion emission is firstly accomplished by Erbium ions absorbing the pump photons to populate the $^2I_{9/2}$ excited level. Then these ions relax into the $^4I_{11/2}$ level, further. The Erbium ions in the $^4I_{11/2}$ level is either de-excited down to the metastable $^4I_{13/2}$ level responsible for the laser transition around 1535 nm or down to the fundamental level $^4I_{15/2}$ in emitting 976 nm photons. Long lifetime of the metastable $^4I_{13/2}$ level allows further excited up wards to the $^4S_{3/2}$ level by absorbing pumping photons. It should be noticed that both nonradiative decays of $^4I_{9/2}\rightarrow{}^4I_{11/2}$ and $^4I_{11/2}\rightarrow{}^4I_{13/2}$ through multiphonon interaction are the source of the temperature rise of the microspheres.

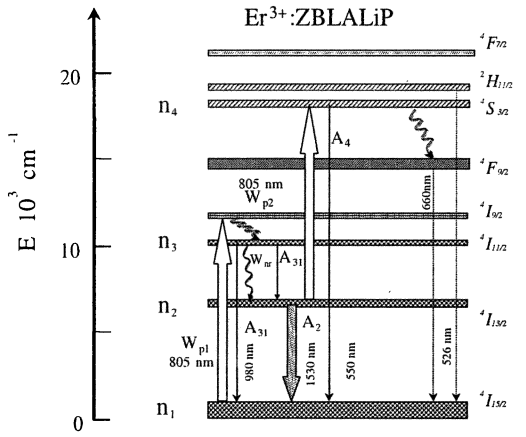

Fig5. Partial Energy-level diagram and the associated transition processes of Er^{3+}:ZBLALiP pumped at around 805nm.

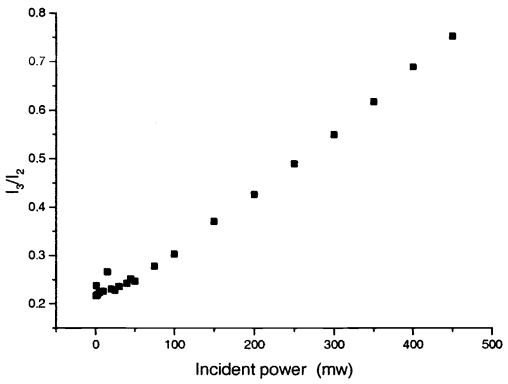

Fig.6 Dependence of the green emission intensity ratio on the incident pump power for the Er:ZBLALiP microsphere.

We use the upconversion intensity ratio originated from the levels 2 ($^4S_{3/2}$) and 3 ($^2H_{11/2}$), which are responsible for the green emission, to calibrate the microsphere temperature. The physical mechanism is the same as described in ref. 2: The multiphonon relaxation rate is inversely proportional to the number of phonons N necessary to span the energy gap between the $^4S_{3/2}$ and $^4F_{9/2}$. In reality, the energy gap between the levels of 2 and 3 is about 800 cm^{-1}, comparable to the value of $k_BT\approx200$ cm^{-1}, and much less than the energy gap between them and the nearest lower level $^4F_{9/2}$, about 3200 cm^{-1} (at least seven phonons to bridge this energy gap). This fact leads to a quasi-thermal population distribution in the

manifolds of 2 and 3 due to strong phonon interaction (typically incorporating one or two phonons) between them. The ratio of the emission intensities originating from the levels 3 and 2 can thus be expressed by the following equation[2]

$$\frac{I_3}{I_2} = \frac{A_3 g_3 h\upsilon_3}{A_2 g_2 h\upsilon_2} \cdot \exp\left[-\frac{E_{32}}{k_B T}\right], \tag{1}$$

where ν_2 and ν_3 are green emission frequencies, g_2 and g_3 the degeneracies (2J+1), and A_2, A_3 the total spontaneous-emission rates of the level 2 and 3, respectively. E_{32} is the energy gap between the levels 2 and 3.

Because of no spectroscopic data valid up to now for Er:ZBLALiP, exactly calculating eq.(1) is impossible. While eq.(1) allows us to know the dependence of green emission intensity ratio on the inverse of the temperature as an exponential decay function, which can be used to fit the experimental data in Fig.6. In order to calibrate the intensity ratio versus temperature, the green emission spectra from 500 nm to 580 nm of a 6% Er:ZBLALiP were performed from 300 K downwards 160 K, as shown in Fig.7. The green emission intensity ratio versus the inverse of temperature is shown in Fig.8, and exponential decay fit based on eq.(1) yields

$$\frac{I_3}{I_2} = 0.0105 + 4.241 \exp\left[-\frac{981}{T}\right]. \tag{2}$$

Applying eq.(2) to the experimental data in Fig.6 results in calibrating the microsphere temperature in terms of incident power, as represented in Fig.9. From Fig.9, an incident power of 1mw corresponds to microsphere temperature of 325 K, while 450 mw to 562 K. Fig.9 represents the sensing dependence of the green intensity ratio on the microsphere temperature. A prospective application to construct a point temperature sensor (applicable temperature ranging from 100 to 850 K) by tens micrometer-size with fiber-coupling microspheres is reliable.

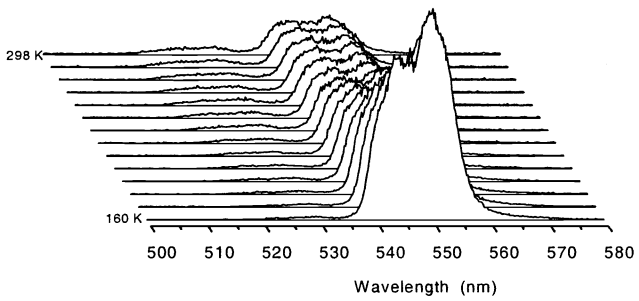

Fig.7 Evolution of green emission spectra with temperature from 298 K downwards to 160 K For 6% Er:ZBLALiP. The temperature change step is about 10 K except 210 K to 190 K. Pump source is kept low level at 488 nm and constant throughout this measurement.

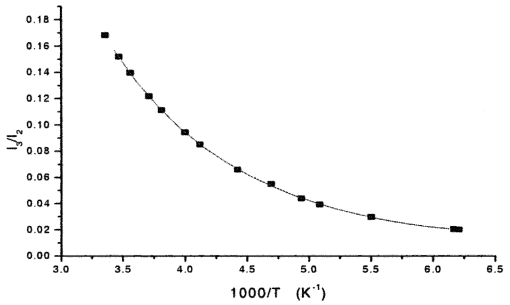

Fig.8 The dependence of green emission intensity ratio on the inverse of microsphere temperature.

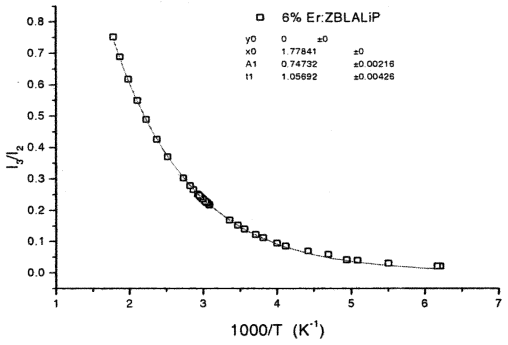

Fig.9 The green intensity ratio as a function of the inverse of the microspherical temperature.

4. CONCLUSION

We present an initial experimental study on thermal properties of an Er:ZBLALiP microsphere excited at 805 nm. The green upconversion emission intensity ratio of 522 nm over 550 nm bands increases from 0.23 to 0.72 under 10 mW and 450 mW pumping levels. Low temperature emission spectra allow us to calibrate green upconversion intensity ratio versus the microsphere temperature, then the sensing dependence of the green intensity ratio on the microsphere temperature is calculated for high temperature range. The point temperature sensor covers wide temperature range from 100 to 850 K, and has only tens micrometer in size and could be integrated with optical fiber.

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