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Highly sensitive and accurate optical thermometer through Er doped tellurite glasses

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ABSTRACT

We investigate the thermal effects of Er^{3+} doped tellurite glasses on the upconversion properties. It is found that the sensitivity of the thermometer based on the FIR technique increases monotonously with the decreasing doping concentration. However, low doping leads to weak upconversion intensity and further decrease the sensing accuracy, which makes it difficult to achieve the high sensitivity and accuracy simultaneously. Influences of the irradiating laser power on the sensing behaviors were studied in the purpose of enhancing the signal intensity. It is found that the heating effect of incident laser (up to hundreds of mW) can be neglected, indicating the feasibility of using high laser power and low doping sample to produce both high sensitivity and high accuracy. In addition, this paper respectively discusses the mechanisms of the upconversion processes and the concentration dependent sensitivity.

1. Introduction

Considerable attention has been attracted on upconversion photoluminescence (UC-PL) of rare earth (RE) ions doped vitreous hosts which emit high energy photons after the absorption of two or more low energy photons. Vitreous hosts, on one hand, are readily to be manufactured into various desirable shapes and thus can be utilized in different applications, such as laser materials, optical fibers, planar waveguides, or other photoelectric devices. On the other hand, emission bands of rare earth ions undergo significantly widening compared to crystal matrix, which is due to the complex environments of glass [1] that makes rare earth ions doped glasses to be promising materials for optical amplifier, optical data storage and communication engineering [2–5].

Among the vitreous hosts, TeO_2 based glasses, with low melting temperature, decrease the cost and increase the synthesizing feasibility. Especially, low phonon energy of tellurite glass also leads to higher UC-PL efficiency [6,7]. Tellurite glasses possess superior corrosion resistance and stability [8], despite the fact that it is not as efficient as the well-known fluoride glasses.

Alternatively, optical thermometer based on the fluorescence intensity ratio (FIR) technique, not being impacted by the fluctuation of laser power or the induction of surrounding electromagnetic, have shown unique potentials for tissue thermal sensing [9–11]. Especially, enhancing the sensitivity of thermometer carries vital importance for monitoring the slight temperature change during some special processes, such as temperature-dependent drug release [12] and photothermal therapy [13]. Many efforts have been made to achieve high sensitivity thermometer on the basis of upconversion emissions [14–17]. To date, the state-of-the-art materials reach to nearly 0.03 K^{-1} and more than 1% K^{-1} for absolute sensitivity and relative sensitivity, respectively [18–23]. However, sensing sensitivity of upconversion thermometer in vitreous hosts remains relatively low [24]. Thus it is still necessary to achieve the highly sensitive temperature sensing in vitreous hosts, in the purpose of fitting the high sensitive temperature sensing applications of upconversion glasses.

In this paper, we synthesized tellurite glass samples with different Er^{3+} doping concentrations, and investigated the upconversion mechanisms of these samples on the basis of the spectral measurements. Besides, temperature sensing behaviors of different samples were carefully studied on the basis of FIR method.

2. Experimental

2.1. Synthesis of Er^{3+} doped tellurite glasses

TeO_2 (99.99%), ZnO (99.9%), ZnF_2 (99.9%) and ErF_3 (99.99%) were used as received. Er^{3+} doped tellurite glasses were prepared using

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conventional melt quenching method as follows. 10 mmol raw materials with a mole ratio of xErF$_3$-(74.6-x)TeO$_2$-8.8ZnO-16.6ZnF$_2$ (x = 0.1, 0.2, 0.4, 0.8, 1, and 2) were weighed and ground thoroughly. After being transferred into a ceramic crucible, the mixture was sintered in an electrical furnace at 850 °C for 30 min, and the vitreous liquid was poured onto a copper mould which was preheated to 250 °C. After annealing for 17 h, the samples were cut and carefully polished to form two smooth sides with a thickness of about 2 mm for spectral measurements.

2.2. Experimental setups

For the spectral measurements, near infrared laser with a central wavelength of 976 nm (7 W, Lasever Optoelectronic Technology Co. Ltd.) was collimated using a battery of lens (with a spot diameter of about 1 mm). UC-PL signals were collected by a monochromator (Omni λ-500, Zolix Instruments Co. Ltd.) equipped with a photomultiplier tube (CR131, Zolix Instruments Co. Ltd.). Samples were attached onto a heating stage (JK-HP-130B, Jingke Scientific Instrument Co. Ltd.) with the temperature resolution of 0.1 K. The setting temperature of the stage ranged from room temperature to 200 °C. Meanwhile the actual temperatures of samples were measured by a thermocouple (HH12B, Omega, Co. Ltd.) attached onto the surface of the glasses. During the measurement, time interval of the spectral collection was 20 min, ensuring the thermal equilibrium of samples.

3. Results and discussion

3.1. Upconversion properties

Fig. 1a shows the UC-PL spectra of samples doped with various Er^{3+} concentrations. Under the excitation of 976 nm laser, green and red emissions are observed in all samples with a relatively large range of Er^{3+} concentration from 0.1 to 2 mol%. The two green emission bands (510–535 nm and 535–570 nm) are the transitions of Er^{3+} $^2H_{11/2}$ and $^4S_{3/2}$ levels to the ground state $^4I_{15/2}$ level, and the red band (640–680 nm) is aroused from the transition of Er^{3+} $^4F_{9/2}$ to $^4I_{15/2}$ energy level (Fig. 2).

The possible pathways of Er^{3+} upconversion processes are shown in Fig. 2. Er^{3+} ion absorbs two NIR photons continuously and is excited to $^4I_{11/2}$ and $^4F_{7/2}$ states successively by GSA and ESA2, then Er^{3+} ions in $^4F_{7/2}$ state populate the $^2H_{11/2}$ and $^4S_{3/2}$ states by nonradiative relaxation, the green emission arises. In addition, another mechanism responsible for the green population is the cross relaxation process CR1, which is the interaction between neighboring Er^{3+} ions. As for the red emission, three main mechanisms can be concluded as follows: 1. Decay of $^4S_{3/2}$ state to $^4F_{9/2}$ state because of nonradiative relaxation; 2. CR2 process of $^4F_{7/2}$ and $^4I_{11/2}$ states populating $^4F_{9/2}$ state; 3. ESA1 of Er^{3+} ions from $^4I_{13/2}$ level to $^4F_{9/2}$ state.

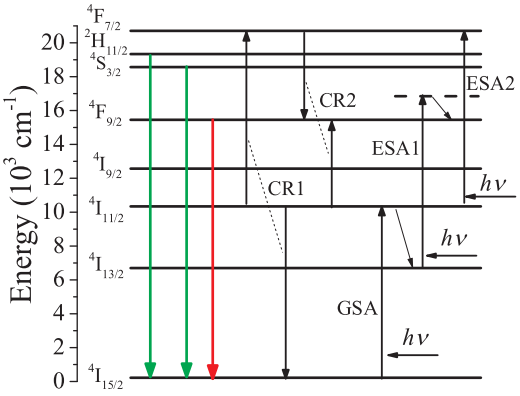

Fig. 2. Schematic of the pathways of Er^{3+} upconversion processes.

The variations of UC-PL intensity with Er^{3+} contents are shown in Fig. 1b. With the increase of Er^{3+} doping concentration, the integral intensity rises firstly until reaching its maximum at 1 mol%, and then declines. It is reasonable that the intensity rises due to the increased number of luminescent centers. As for the declined intensity at higher doping levels, UC intensity tends to be quenched by the energy transfer (ET) processes (including the transfer between neighboring ions and the transfer from ions to the defects inside/outside the matrix), which is the so-called concentration quenching effect. Thus the decreased intensity can be attributed to the above mentioned concentration quenching effect. It should be noted that although the obvious concentration quenching shows for green emission, the red intensity increases monotonously with increasing the dopant concentration. This should be aroused by the CR2 process $^4F_{7/2}+{}^4I_{11/2}\rightarrow{}^4F_{9/2}+{}^4F_{9/2}$, which populates the red emission level and is highly sensitive to the dopant concentration. The CR process is dominant for the red upconversion emission, thus the quenching effect become less effective.

In addition, the intensity of green emission is dominant compared to the red one, which can be attributed to the low phonon energy of the host materials. Low energy phonons suppress the decay process from green level to the red one ($^4S_{3/2}\rightarrow{}^4F_{9/2}$). Meanwhile, the ESA1 process is also restrained as more phonons are required to bridge the energy mismatch of the incident photon energy and the energy gap between $^4F_{9/2}$ and $^4I_{13/2}$ level.

In order to clarify the UC-PL mechanisms of Er^{3+}, upconversion power dependence, showing the variations of upconversion intensity with irradiated laser power (in the double logarithmic form), are measured. As shown in Fig. 3, all the power dependent curves can be fitted linearly, except some data points at high excitation power range. As is well known, high ambient temperature intensifies the nonradiative decay processes due to the increased state density of the

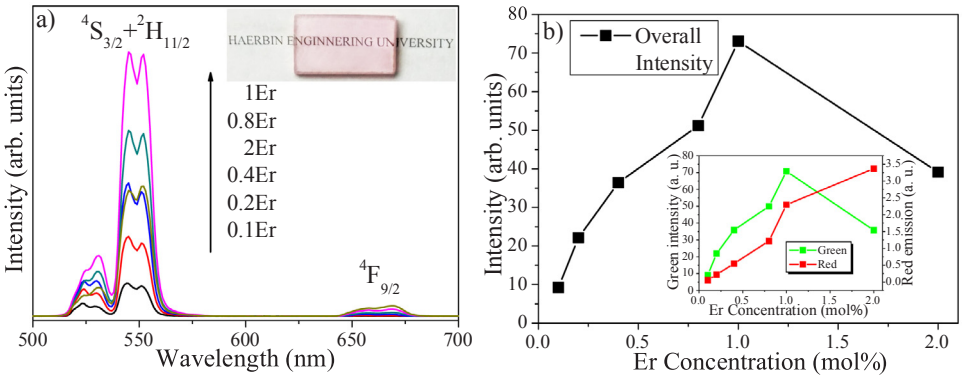

Fig. 1. a) Upconversion spectra of samples doped with various Er^{3+} concentrations. The inset is the digital photograph of the glass; b) variations of UC-PL intensity with Er^{3+} contents.