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Optical thermometry based on up-conversion luminescence of Tm^{3+} doped transparent Sr_2YF_7 glass ceramics

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ABSTRACT

Tm^{3+}/Yb^{3+} co-doped transparent glass ceramics (GC) containing Sr_2YF_7 nanocrystals were successfully manufactured by traditional melt-quenching technique. Their structural and up-conversion luminescent properties were systemically investigated through X-ray diffraction (XRD), transmission electron microscope (TEM) and a series of spectroscopy methods. Tremendously enhanced up-conversion emissions with obvious Stark splitting and prolonged luminescence lifetime were observed after crystallization. These optical spectroscopy results manifest that Tm^{3+} ions have incorporated into the Sr_2YF_7 crystalline lattice with low phonon energy (~ 400 cm^{-1}) after heat-treatment. The $^3F_{2,3}$ and $^3H_4$ levels of Tm^{3+} can be explored as thermally coupled energy levels (TCEL) for temperature sensing because of their befitting energy gap (~ 2000 cm^{-1}). At the same time, the population of $^1G_4$ state of Tm^{3+} is indirectly originated from $^3H_4$ one. Therefore the temperature sensing performances of Tm^{3+} doped Sr_2YF_7 GC were investigated by fluorescence intensity ratio (FIR) between $^3F_{2,3} \rightarrow {}^3H_6$ and $^1G_4 \rightarrow {}^3F_4$ up-conversion emissions of Tm^{3+}. Results show that the theoretical maximum value of relative sensitivity $S_{R\text{-max}}$ is 1.16%K^{-1} at 428 K, and absolute sensitivity S_A keeps increasing with temperature. Such Tm^{3+}/Yb^{3+} co-doped Sr_2YF_7 GC may be excellent candidate for optical temperature sensors.

1. Introduction

Recently, optical temperature sensors, types of non-contact temperature sensors, have been investigated widely due to their potential applications in electrical power station, oil refineries, building fire detection and biocompatible temperature probe [1–13]. Compared to conventional contact temperature sensors, optical temperature sensors have high sensitivity, short response time and can be used in corrosively, electromagnetically and thermally special environment [5,8]. Optical temperature sensors are based on optical techniques of luminescent materials, such as fluorescence lifetime, amplified spontaneous emissions and fluorescence intensity ratio (FIR) [7–9]. Among these optical based techniques, FIR technique has been regarded as a promising approach for temperature sensing because of their intrinsic advantages of high reliability, improved measurement accuracy and broad operating temperature range [5]. This technique is built on temperature dependent emissions form thermally coupled energy levels (TCEL), which makes it can avoid the influences of spectrum losses and fluctuations in excitation intensity [14–16].

Rare earth (RE^{3+}) ions (such as Eu^{3+}, Er^{3+}, Ho^{3+}, Tm^{3+}) were usually used as active centers for temperature sensing based on FIR technique owing to the different dependences of their electronic transitions on temperature [10,16–18]. Among these RE^{3+} ions, Er^{3+} ion is one of the most sensitive probe in optical temperature sensing [19–21]. The up-conversion FIR value of Er^{3+} TCEL ($^2H_{11/2}$ and $^4S_{3/2}$) varies with the temperature notably, which can be acted as index of temperature [16]. Unfortunately, it is difficult to avoid the spectra overlap of emission bands from Er^{3+} TCEL for their small energy gap (~ 720 cm^{-1}), which may impact the measurement resolution [22].

Tm^{3+} ion can overcome the intrinsic shortcoming of Er^{3+}. As shown in Fig. 1, $^3F_{2,3}$ and $^3H_4$ levels of Tm^{3+} are chosen as TCEL because their energy gap (~ 2000 cm^{-1}) is suitable and larger than that of Er^{3+} [22]. In fact, the population of $^1G_4$ and $^1D_2$ states of Tm^{3+} are indirectly originated from $^3H_4$ one. Hence, the up-conversion FIR of transitions from $^3F_{2,3}$ and other three levels ($^1D_2$, $^1G_4$, $^3H_4$) of Tm^{3+} ions can be applied in temperature detecting [4].

Generally, host materials with lower phonon energy and excellent stability will benefit the performances of optical temperature sensors. Hosts with lower phonon energy will show higher luminescent efficiencies, which will result in higher measurement accuracy [5,15]. The

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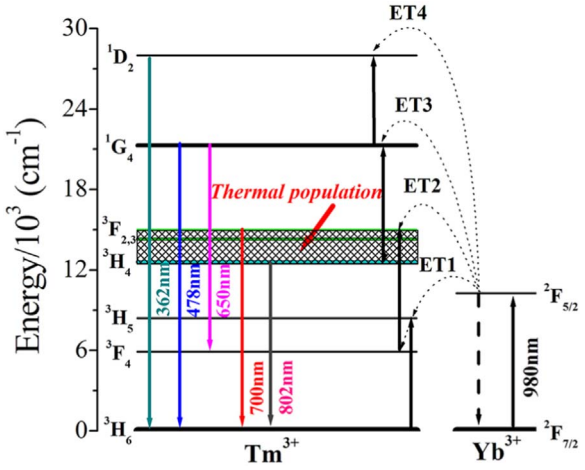

Fig. 1. Energy level diagrams of Tm^{3+} and Yb^{3+} ions as well as the possible up-conversion mechanisms and temperature' detector mechanism.

excellent stability of hosts makes them can be used in high temperature and other special environment [23]. Transparent oxyfluoride glass ceramics (GC) are composite materials that containing fluoride nanocrystals phase and oxide glass phase [24–26]. These materials are generally achieved by controlling crystallization process of precursor glass with specially designed chemical compositions [26–28]. They combine the advantages of good stability of oxide glass and low phonon energy (~ 400 cm^{-1}) environment of fluoride nanocrystals, which can be appropriate matrices for optical temperature sensors [5,14,16].

Tetragonal Sr_2YF_7 is an important matrix for RE^{3+} ions to fabricate up-conversion or downshifting phosphors because of its low phonon energy, similar ionic radius and identical coordination of Y^{3+} and RE^{3+} ions [29–32]. Recently, RE^{3+} doped Sr_2YF_7 nanoparticles have attracted much attention [29–31]. Chen et al. reported the syntheses of monodisperse and size-controllable Sr_2YF_7:RE^{3+} nanoparticles and investigated the up-conversion properties. Their results revealed great potential of Sr_2YF_7: RE^{3+} nanoprobes in practical bioassays for cancer diagnosis [31]. At the same time, tetragonal Sr_2YbF_7:Er^{3+} GC present excellent structure, up-conversion and temperature sensing properties [5]. Therefore, we believe that the tetragonal Sr_2YF_7 GC doped with Tm^{3+} will show excellent temperature sensing performances.

In this work, Tm^{3+}/Yb^{3+} co-doped transparent Sr_2YF_7 GC were successfully manufactured. Under 980 nm laser excitation, the emission intensity of Tm^{3+} was highly enhanced after heat-treatment. Temperature-dependent up-conversion from $^3F_{2,3}$ and $^1G_4$ levels of Tm^{3+} were systemically investigated to explore their potential application in temperature detecting. The theoretical max relative sensitivity $S_{R\text{-max}}$ of 1.16% K^{-1} is achieved at 428 K and the absolute sensitivity S_A keeps increasing with temperature. All results show that Sr_2YF_7:Tm^{3+}/Yb^{3+} GC have greatly possible application in optical temperature sensors.

2. Experimental

Glass samples with nominal composition $70SiO_2$-$7Al_2O_3$-$16SrF_2$-$7YF_3$-$0.5YbF_3$ −$0.1TmF_3$ (in mol%) were prepared through high temperature melt-quenching route. SiO_2, Al_2O_3, SrF_2 (A.R., all from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) and high purity YF_3, YbF_3, TmF_3 (99.99%, from AnSheng Inorganic Materials Co., Ltd., Ganzhou, Jiangxi, China) were used as starting materials. The well ground stoichiometric chemicals were put into an alumina crucible and melted at 1550 °C for 1 h in air atmosphere. The melt was poured onto a 300 °C preheated stainless-steel plate and then pressed quickly by another plate to get solid samples. After annealed at 450 °C for 3 h to release internal stress, precursor glass (labeled as PG) were formed. Subsequently, PG was heat-treated for 2 h at 750 °C to elaborate transparent glass ceramics, which was labeled as GC. Finally, the obtained specimens were cut and polished to plates of about 15 × 10 × 1.8 mm^3 in size for further measurements.

X-ray diffraction (XRD) patterns were performed on a Philips X'Pert PRO SUPER X-ray diffraction apparatus (Almelo, the Netherlands) with CuKa radiation (λ = 0.154056 nm) over the angular range 10° ≤ 2θ ≤ 80° in a step size of 0.0167°. PG and GC samples were ground into powder for XRD measurement. Transmittance spectra were measured on a Hitachi U-3900 Ultraviolet-Visible (UV–vis) spectrophotometer (Tokyo, Japan). The microstructure of GC sample was analyzed by a JOEL JEM-2010 transmission electron microscopy (TEM) (Tokyo, Japan). Up-conversion spectra were measured with an Edinburgh FS920 spectrofluorometer (Livingston, UK) with a 980 nm laser as excitation source. The spot size of laser was about 1 × ×6 mm^2. And the pump power was adjusted through neutral density filters. Lifetime measurements were recorded on an Edinburgh FS5 spectrofluorometer equipped with a tunable PSU-111-LED 980 nm pulse laser as the excitation source. Temperature of GC sample fixed on a copper post was controlled over the range of 303–663 K by a temperature controller (FOTEK MT48-V-E, Taibei, Taiwan) with a type-K thermocouple and a heating tube.

3. Results and discussion

3.1. Structural analyses of samples

The XRD patterns of PG and GC samples are shown in Fig. 2(a). Obviously, PG exhibits a very weak diffraction peak over diffuse humps and the diffuse humps are attributed to amorphous glass phase. Several intense diffraction peaks are observed in XRD patterns of GC sample. These diffraction peaks are corresponding to tetragonal Sr_2YF_7 nanocrystals (JCPDS no. 53-0675), which indicates the formation of Sr_2YF_7 nanocrystals in GC sample. And the doping of RE^{3+} ions does not change the lattice structure of Sr_2YF_7 nanocrystals due to their similar ionic radius and identical valence state. The mean size of Sr_2YF_7 nanocrystals in GC can be estimated by Scherer's equation [14],

$$D = k\lambda/\beta cos\theta \quad (1)$$

where $k = 0.89$, λ (= 0.154056 nm) represents the wavelength of CuKa radiation, θ is Bragg angle and β represents the corrected half-width of diffraction peak. The mean size of Sr_2YF_7 nanocrystals in GC is estimated to be 16 nm.

The transmittance of GC is dependent on the size of nanocrystals. Generally, the smaller size of nanocrystals in GC, the higher transparency of GC is [33]. The size of Sr_2YF_7 nanocrystals in present GC is about 16 nm, which is much smaller than the wavelength of VIS light. Therefore, PG and GC samples both hold a high transparency up to 80% in VIS light region, as shown in Fig. 2(b). There are two evident absorption peaks located at 680 and 790 nm, which are corresponding to the transitions of Tm^{3+} ions from $^3H_6$ ground state to $^3F_{2,3}$ and $^3H_4$ excited states, respectively [34].

The TEM and HRTEM images of GC sample are displayed in Fig. 2(c) and (d), respectively. TEM bright-field micrograph clearly shows that 10–20 nm sized nanocrystals homogeneously distributed in the glass matrix, which is in agreement with the result estimated by Scherer's equation. Selected area electron diffraction (SAED) patterns (inset of Fig. 2(c)) prove that the obtained GC is composite material that containing polycrystalline phase and glass phase. HRTEM image displays well-defined lattice fringes of Sr_2YF_7 nanocrystals. The associated interplanar distance d value calculated through two separated crystal planes is about 0.333 nm, which can be indexed to the (302) crystal plane of tetragonal Sr_2YF_7 ($d_{(302)}$ = 0.330 nm).

3.2. Up-conversion luminescence and mechanism

Fig. 3(a) exhibits the up-conversion spectra (λ_{ex} = 980 nm) of PG