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Synthesis and thermometric properties of Yb^{3+}-Er^{3+} co-doped K_2GdF_5 up-conversion phosphors

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Abstract: Yb^{3+}-Er^{3+} co-doped K_2GdF_5 up-conversion phosphor was successfully synthesized by a solid-state reaction method. The phase purity and structure of the sample were characterized by powder X-ray diffraction. The sample emitted orange light at room temperature and its up-conversion spectra at different temperatures were recorded under the excitation of a 980 nm diode laser. The energy transfer from Yb^{3+} to Er^{3+} notably enhanced the up-conversion luminescence intensity. The possible up-conversion mechanisms and processes were proposed based on the power dependence of the luminescence intensities. The temperature-dependent up-conversion luminescence and temperature sensing performances of the sample were discussed according to the fluorescence intensity ratio of green emissions originating from $^2H_{11/2}/^4S_{3/2}\rightarrow{}^4I_{15/2}$ transitions of Er^{3+} in the range from 307 K to 570 K under the excitation of 980 nm laser with power of 260 mW. The dependence of the fluorescence intensity ratio on temperature was fitted with an exponential function and the effective energy difference obtained was 690 cm^{-1}, which further gave a relative temperature sensitivity of 1.1%/K at 307 K. The results suggested that the Yb^{3+}-Er^{3+} co-doped K_2GdF_5 sample is a promising candidate for optical temperature sensor.

Keywords: up-conversion luminescence; fluorescence intensity ratio; sensitivity; rare earths

Over the past few years, lanthanide-doped up-conversion (UC) luminescent materials have been widely investigated[1–9]. These up-conversion materials have shown potential applications in diverse fields because of their unique optical properties, including narrow emission bandwidth, large anti-Stokes shift, long luminescence lifetime and high photostability[10–12]. UC phosphors show a possibility of excitation by near infrared lasers, such as 980 or 808 nm lasers, which can penetrate biological media without auto-fluorescence. Therefore, UC phosphors are suitable for the applications in bio-imaging labeling, biological sensing and photo-activated therapeutic agents.

Temperature is one of the most important physical variables affecting the dynamic and viability of practically all natural and engineered systems. Optical thermometry based on the fluorescence intensity ratio (FIR) technique using temperature-dependent UC luminescence intensities from two thermally coupled energy levels of rare earth ions has attracted increasing attention[13–16]. Yb^{3+}- Er^{3+} co-doped UC luminescent materials have been extensively investigated as potential optical temperature sensors because of the thermally coupled energy levels ($^2H_{11/2}$ and $^4S_{3/2}$) of Er^{3+} and intense broad absorption of Yb^{3+} [17]. The effective energy transfer (ET) from Yb^{3+} to Er^{3+} under the excitation of 980 nm near-infrared laser can easily occur[18]. Yb^{3+}-Er^{3+} co-doped UC luminescent materials are regarded as an ideal choice for detection of temperature in biology.

About the fluoride host K_2GdF_5, there are only a few studies on the visible quantum cutting and the thermoluminescence of K_2GdF_5:Tb^{3+} [19–21], energy transfer from Pr^{3+} to Eu^{3+} in K_2GdF_5:Pr^{3+} [22] and near ultraviolet to near infrared luminescence spectroscopy of K_2GdF_5:Er^{3+} [23]. To our best knowledge, little work about K_2GdF_5:Yb^{3+}, Er^{3+} has been reported in literature. In this work, a well-crystallized orthorhombic K_2GdF_5:18 mol.%Yb^{3+},2 mol.%Er^{3+} powder sample was synthesized in view of its low cut-off phonon energy of about 475 cm^{-1} [24]. Under 980 nm excitation, the UC spectra were first studied at different temperatures from 307 to 570 K. The results demonstrate that this material is a promising candidate for temperature sensing.

1 Experimental

The K_2GdF_5:18 mol.%Yb^{3+},2 mol.%Er^{3+} sample was prepared by the solid state reaction from a stoichiometric mixture of KF (analytical reagent) and LnF_3 (Ln=Gd, Yb and Er, purity of 99.99%). The raw materials were thor-

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oughly ground and heated at 600 ºC for eight hours in a sealed quartz tube under a protective atmosphere (95% N_2 and 5% H_2)[19]. The material was cooled to room temperature and then crushed into fine powders.

The phase identification of the K_2GdF_5:18 mol.%Yb^{3+},2 mol.%Er^{3+} sample was characterized by an X-ray diffractometer (Rigaku-TTR-III), using nickel-filtered Cu Kα radiation (λ=0.15418 nm) in the 2θ range from 10º to 70º. The UC spectra excited by a 980 nm diode laser were recorded by a Jobin-Yvon HRD-1 double monochromator equipped with a Hamamatsu R928 photomultiplier. The signal was analyzed by an EG&G 7265 DSP Lock-in amplifier. The size of the irradiated spot is about 2 mm×4 mm and the output pump power of the laser was adjusted by neutral density filters. Temperature of the sample fixed on a copper post was controlled over the range of 300–773 K by a temperature controller (FOTEK MT48-V-E) with a type-K thermocouple and a heating tube.

2 Results and discussion

2.1 Structure properties

As shown in Fig. 1, the main diffraction peaks of our sample agree well with the standard powder diffraction file 77-1924, indicating that K_2GdF_5:18 mol.%Yb^{3+},2 mol.%Er^{3+} has been successfully synthesized.

Fig. 2 presents the crystal structure of K_2GdF_5 and the coordination polyhedrons of anions around K^+ and Gd^{3+} cations. The structure was modelled through a program called Diamond. K_2GdF_5 crystallizes in the orthorhombic structure with space group of *Pnma*. The K^+ ion is surrounded by eight F^- anions. Each Gd^{3+} ion lies in a D_{2h} symmetry site and is connected to seven F^- anions forming a GdF_7 polyhedron. The polyhedrons are connected by a common edge and form a chain paralleling to the c axis. This one dimensional structure of the sample has great influence on the energy transfer properties among Gd^{3+} sub-lattices[19].

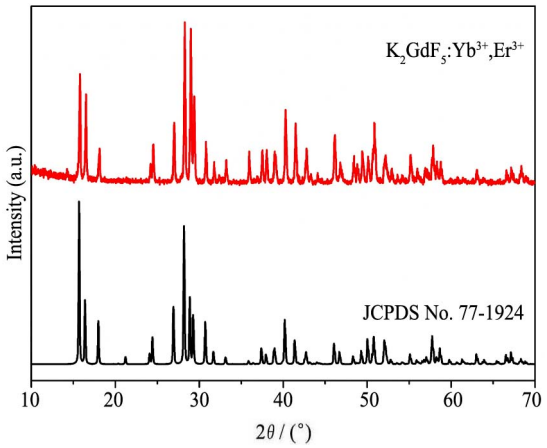

Fig. 1 XRD pattern of the as-prepared K_2GdF_5:18 mol.%Yb^{3+}, 2 mol.%Er^{3+} powder sample and the standard data of K_2GdF_5 (JCPDS No. 77-1924)

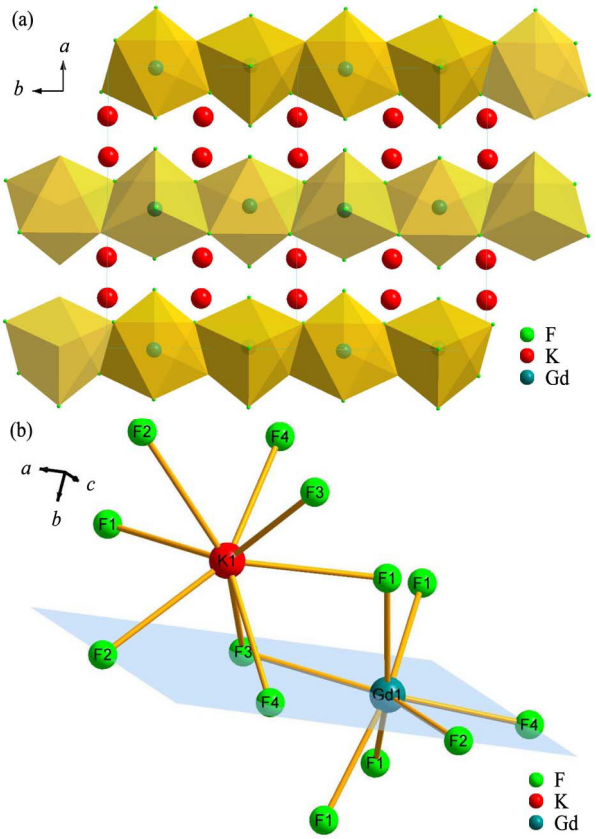

Fig. 2 Crystal structure of K_2GdF_5 (a) and the coordination polyhedron of anions around K^+ and Gd^{3+} cations (b)

2.2 Energy level scheme and mechanism of UC emission

The UC emission intensity (I) depends on the pump laser power (P) with a formula: $I \propto P^n$, where n is the number of pumping photons involved in the UC process. In order to have a better understanding of the possible UC processes and the mechanisms of the green and red emission in Yb^{3+}-Er^{3+} co-doped K_2GdF_5 sample, the double logarithmic diagrams of UC emission intensity for bands at 545 nm (corresponding to $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition) and 669 nm (corresponding to $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition) as a function of pump power are presented in Fig. 3(a). The experimental data and fitting curves reflect the relationship between the integrated UC intensities and the pump power for the Yb^{3+}-Er^{3+} co-doped K_2GdF_5 sample. As shown in Fig. 3(a), it can be found that the slopes of both green and red emissions are 1.93, which is close to 2.0 within the margin of error, indicating that both the transitions of $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ are two-photon process.

The possible UC processes are schematically illustrated in Fig. 3(b). Under the 980 nm excitation, Yb^{3+} absorbs an infrared photon and transits from ground state $^2F_{7/2}$ to excited state $^2F_{5/2}$. The intermediary $^4I_{11/2}$ level of Er^{3+} is populated through ET process: $^4I_{15/2}$ (Er^{3+})+$^2F_{5/2}$ (Yb^{3+})$\rightarrow {}^4I_{11/2}$ (Er^{3+})+$^2F_{7/2}$ (Yb^{3+}) or ground state absorption: $^4I_{15/2}$ (Er^{3+})+a photon (980 nm)$\rightarrow {}^4I_{11/2}$ (Er^{3+}). Be-