Radiation Measurements 90 (2016) 298–302

Contents lists available at ScienceDirect

Radiation Measurements

journal homepage: www.elsevier.com/locate/radmeas

High-temperature VUV spectroscopy of KYF_4 crystals doped with Nd^{3+}, Er^{3+} and Tm^{3+} ions

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HIGHLIGHTS

- Quenching temperatures of 5*d*-4*f* luminescence from Nd^{3+}, Er^{3+}, Tm^{3+} in KYF_4 obtained.
- Thermal quenching for Nd^{3+} and Er^{3+} is caused by non-radiative 5*d*-4*f* transitions.
- Thermal quenching for Tm^{3+} is due to ionization of 5*d* electrons to conduction band.
- Obtained activation energy of thermal quenching of Tm^{3+} 5*d*-4*f* luminescence is 0.66 eV.
- The method for the estimation of energy gap '5*d* level – conduction band' is proposed.

ARTICLE INFO

Article history:
Received 22 October 2015
Received in revised form
16 December 2015
Accepted 19 December 2015
Available online 22 December 2015

Keywords:
5*d*-4*f* luminescence
Thermal quenching
Nd^{3+}
Er^{3+}
Tm^{3+}
KYF_4

ABSTRACT

Thermal quenching of 5*d*-4*f* luminescence from Nd^{3+}, Er^{3+} and Tm^{3+} ions doped into KYF_4 crystals has been investigated in the temperature range up to ~750 K where this luminescence is completely quenched. The obtained temperatures of thermal quenching (T_q) are ~270, 495, 450 K for Nd^{3+}, Er^{3+}, Tm^{3+}, respectively. At high temperatures, thermal quenching of 5*d*-4*f* luminescence from Nd^{3+} and Er^{3+} is accompanied by the appearance of 4*f*-4*f* luminescence from the lower-energy 4*f* levels. It has been shown that the dominating mechanism of thermal quenching for Nd^{3+} and Er^{3+} ions is thermally stimulated non-radiative transitions (intersystem crossing) from the 5*d* states to lower-energy 4*f* levels, namely $^2G(2)_{9/2}$ and $^2F(2)_{7/2}$, respectively, whereas for the Tm^{3+} ion, thermally stimulated ionization of 5*d* electrons to the conduction band states is responsible for thermal quenching of 5*d*-4*f* luminescence. The energy gap between the lowest Tm^{3+} 5*d* level and the bottom of the KYF_4 conduction band has been estimated to be 0.66 eV.

1. Introduction

It is well known that some trivalent lanthanide (Ln) ions show radiative decay of their mixed $4f^{n-1}5d$ electronic states, i.e. such Ln^{3+} ions demonstrate 5*d*-4*f* luminescence (Yang and DeLuca, 1976; Wegh and Meijerink, 1999; Makhov et al., 2001; Kirm et al., 2007). This luminescence is caused by transitions from the lowest level of the $4f^{n-1}5d$ electronic configuration (hereafter – the lowest 5*d* level) to the ground state or some excited levels of the $4f^n$ electronic configuration (4*f* levels) of the Ln^{3+} ion. For the first half of the lanthanide series, transitions from the lowest 5*d* level to the 4*f* levels are spin-allowed (SA) and 5*d*-4*f* luminescence is fast with typical lifetimes in the nanosecond range. In the second half of the series, transitions from the lowest 5*d* state (so-called high-spin (HS) state, with value of spin higher than that in the ground state) are spin-forbidden (SF) (Wegh and Meijerink, 1999), and such SF 5*d*-4*f* luminescence is slow with lifetimes in the μs range. However, depending on the particular ion, the host, and the temperature, SA 5*d*-4*f* luminescence from the higher-lying, so-called low-spin (LS) 5*d* state, with the same value of spin as in the ground state, can coexist with SF 5*d*-4*f* luminescence. Many Ln^{3+} ions, in particular, Nd^{3+}, Er^{3+}, and Tm^{3+}, when doped into a wide band-gap (mostly fluoride) host, emit 5*d*-4*f* luminescence in the vacuum ultraviolet (VUV) spectral range and it is necessary to apply the technique of VUV spectroscopy for experimental studies of this luminescence.

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http://dx.doi.org/10.1016/j.radmeas.2015.12.016
1350-4487/

One of the important characteristics of any luminescent material is its thermal stability which, in particular, restricts practical application of the material under high-power conditions or at elevated temperatures. In Ref. (Khaidukov et al., 2000) the VUV spectroscopy studies of KYF_4 crystals doped with Nd^{3+}, Er^{3+} and Tm^{3+} have been performed but all measurements were done at room temperature. In the present work, temperature dependencies of VUV luminescence due to 5*d*-4*f* transitions of Nd^{3+}, Er^{3+} and Tm^{3+} ions doped into KYF_4 crystals have been investigated experimentally in the wide temperature range from 10 to ~750 K and the mechanisms responsible for the observed thermal quenching of luminescence have been analyzed.

2. Experiment

The measurements were performed at the SUPERLUMI station (Zimmerer, 2007) of HASYLAB at DESY, using synchrotron radiation from the DORIS storage ring for excitation. The spectra of UV/VUV luminescence were recorded with a Pouey-type monochromator (typical spectral resolution $\Delta\lambda = 20$ Å) equipped with a solar-blind photomultiplier tube Hamamatsu R6836.

KYF_4 single crystals doped with Nd^{3+}, Er^{3+} or Tm^{3+} up to 1 cm^3 in size were grown by a direct temperature-gradient method as a result of the reaction of potassium fluoride aqueous solutions with appropriate mixtures of rare earth oxides (99.995% purity) under hydrothermal conditions at temperature of 750 K and pressures of 100–150 MPa (Dubinskii et al., 1990). The phase purity of synthesized samples was verified by XRD analysis and under hydrothermal conditions KYF_4 crystallized in the trigonal crystal system (Le Fur et al., 1992).

It is well known that Ln^{3+} ions from so-called 'yttrium subgroup' (Dy^{3+} – Lu^{3+}) can be introduced into yttrium-based hosts in the wide range of concentrations up to the complete substitution of Y^{3+}. Accordingly, Er^{3+} and Tm^{3+} doped samples were grown with high doping concentrations (5.0 at% of Er^{3+} and 10.0 at% of Tm^{3+}) in order to obtain higher intensity of 5*d*-4*f* luminescence. The 0.3 at% concentration of Nd^{3+} was chosen as close to the optimal one for obtaining the high-quality and large enough single crystals of KYF_4:Nd^{3+}.

The crystals were cleaved in air prior to mounting either on the flow-type liquid helium cryostat for low-temperature measurements or onto a special home-made sample holder for high-temperature measurements (up to 750 K).

3. Results and discussion

Emission spectra of KYF_4:0.3 at% Nd^{3+} measured in the wide temperature range of 20–623 K are presented in Fig. 1. The broad emission bands are due to parity- and spin-allowed interconfiguration $4f^2 5d$-$4f^3$ transitions in Nd^{3+} with the shortest-wavelength band (peaked at 183 nm) corresponding to transitions from the lowest 5*d* level to the ground state multiplet term $^4I_{J=9/2,11/2,13/2,15/2}$ (Khaidukov et al., 2000). The narrow lines arise from parity-forbidden intraconfiguration $4f^3$-$4f^3$ transitions from the $^2G(2)_{9/2}$ level of the Nd^{3+} ion and, in particular, the strongest line is due to spin-allowed $^2G(2)_{9/2} - {}^2H(2)_{9/2}$ transitions. It should be pointed out that the recorded spectra are resolution limited, as the VUV monochromator used for measurements is not designed for high resolution spectroscopy. As can be seen in Fig. 1, Nd^{3+} 5*d*-4*f* luminescence is thermally quenched and the characteristic temperature of thermal quenching (T_q), determined as the temperature at which the emission intensity is decreased by 50% of its maximal value, is ~270 K. On the other hand, Nd^{3+} 4*f*-4*f* luminescence is not observed at low temperatures, but it becomes observable at elevated temperatures and it is quenched under further increase of temperature

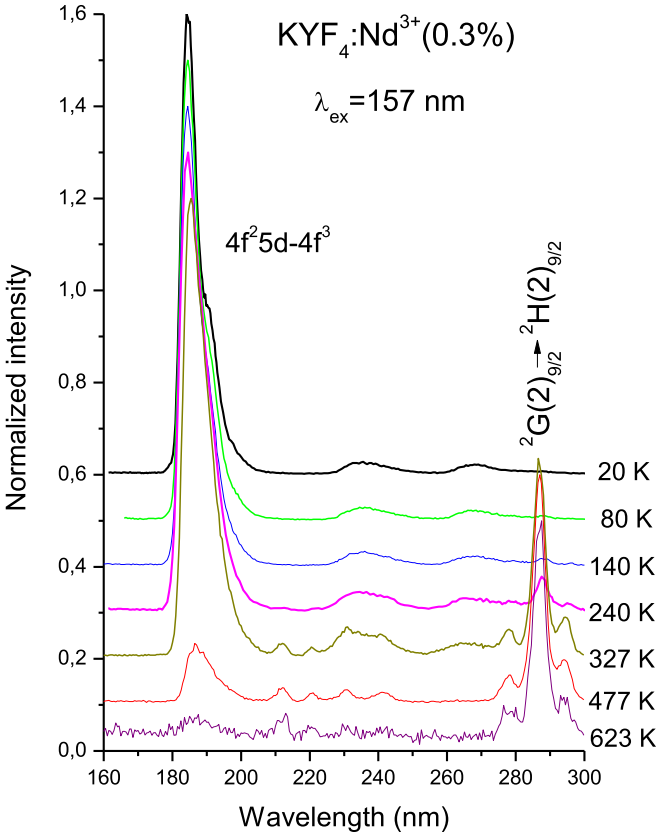

Fig. 1. Emission spectra of KYF_4:0.3 at% Nd^{3+} measured under 157 nm (4*f* – 5*d*) excitation in the temperature range of 20–623 K.

(with $T_q \approx 550$ K).

Emission spectra of KYF_4:5.0 at% Er^{3+} recorded in the temperature range of 10–624 K are shown in Fig. 2. The broad bands correspond to parity-allowed interconfiguration $4f^{10}5d$-$4f^{11}$ transitions while the narrow lines are due to parity-forbidden intraconfiguration $4f^{11}$-$4f^{11}$ transitions from the $^2F(2)_{7/2}$ level of the Er^{3+} ion (Khaidukov et al., 2000). One can see that only slow (SF) 5*d*-4*f* luminescence of Er^{3+} is observed, i.e. in this host very efficient nonradiative relaxation exists from the higher lying LS 5*d* state to the lowest (HS) 5*d* state responsible for SF luminescence (Khaidukov et al., 2000). As in the case of Nd^{3+}, thermal quenching of Er^{3+} 5*d*-4*f* luminescence (with $T_q \approx 495$ K) is accompanied by the appearance of Er^{3+} 4*f*-4*f* luminescence at high temperatures although Er^{3+} 5*d*-4*f* luminescence remains observable at elevated temperatures.

Emission spectra of KYF_4:10.0 at% Tm^{3+} measured in the temperature range of 10–622 K are presented in Fig. 3. The observed broad-band emission is due to parity-allowed interconfiguration $4f^{11}5d$-$4f^{12}$ transitions in Tm^{3+} (Khaidukov et al., 2000). As in the case of Er^{3+} only slow SF 5*d*-4*f* luminescence is detected from Tm^{3+}. In contrast to Nd^{3+} and Er^{3+}, thermal quenching of Tm^{3+} 5*d*-4*f* luminescence (with $T_q \approx 450$ K) is not accompanied by the appearance of narrow-line 4*f*-4*f* luminescence in the studied spectral range which is due to specific energy level structure of Tm^{3+} to be discussed below.

For 5*d*-4*f* luminescence of Ln^{3+} ions the following mechanisms of thermal quenching can be considered (Fig. 4): 1) increase of the probability for multi-phonon non-radiative decay to lower-lying 4*f* levels with temperature (Riseberg and Moos, 1968); 2) thermally stimulated non-radiative transitions (intersystem crossing) from 5*d*