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Eliminating the "decoupling" effect of fluorescence intensity ratio thermometry for an upconversion pumped system

Feng Qin[a,*], Hua Zhao[b], Moyang Lv[c,d], Yuan Zhou[a], Leipeng Li[a], Zhengjia Wang[a], Yangdong Zheng[a], Zhiguo Zhang[a,d,*], Wenwu Cao[a,d,e,*]

[a] Condensed Matter Science and Technology Institute and Department of Physics, Harbin Institute of Technology, Harbin 150080, China
[b] School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China
[c] Harbin Medical University, The Fourth Affiliated Hospital, Harbin 150001, China
[d] Laboratory of Sono- and Photo- Theranostic Technology, Harbin Institute of Technology, Harbin 150001, China
[e] Department of Mathematics and Materials Research Institute, The Pennsylvania State University, PA 16802, USA

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ABSTRACT

To eliminate the "decoupling" effect, which causes the fluorescence intensity ratios (FIR) to deviate from the pure Boltzmann distribution law, a correcting method for an upvonversion pumped system was theoretical derived and experimentally verified. Theoretical results indicated that the double exponential decay of the lower level was entirely involved in the decay of the upper level, which could be used to determine the thermal population degree (η). Taking Tm^{3+} ions as examples, by analyzing the temperature dependence of the fluorescent dynamic curves originating from the thermally coupled pair, the η values at different temperatures were obtained and the corresponding correcting curve is given. The corrected FIR abides by the Boltzmann law, even in the lower temperature range.

1. Introduction

The fluorescence intensity ratio (FIR) technique, based on fluorescent emissions from a thermally coupled pair of rare-earth ions in a crystal matrix, exhibits excellent potential in non–contact temperature sensing applications [1–4]. However, for some thermally coupled pairs, when there are other populating processes besides the thermal populating process, the resulting temperature dependence of FIR exhibits a deviation from the Boltzmann law [5–7]. The deviation originates from the breaking of the expected thermally populating law by a non-thermal population, which is called the "decoupling" effect [5].

For a simple downconversion populated system, such as the $^5D_0$ & $^5D_1$ levels of Eu^{3+}, which was usually pumped by a short wavelength light, a method has been established theoretically to eliminate the "decoupling" effect [6]. By introducing a correcting parameter known as the thermal population degree (η), the conventional FIR may be corrected to follow the Boltzmann law using the η factor:

$$FIR^* = \eta FIR = A \exp\left(-\frac{\Delta E}{kT}\right), \quad (1)$$

where the FIR* is the Boltzmann law satisfied fluorescence intensity ratio. Further, the method of determining the η values was proposed, and the FIR between the $^5D_0$ & $^5D_1$ levels of Eu^{3+} was accordingly corrected. Experimental results verified the effectiveness of the method for a simple downconversion populated system [8]. In this work, the correcting method for an upconversion populated system, which was usually pumped by infrared diode laser, is proposed.

Tm^{3+}/Yb^{3+} co-doped system, as a typical upconversion pumped system, has been extensively investigated for photoluminescence and exhibits promising potential in making optical temperature sensors [9–11]. Above all, the fluorescence efficiency is high, can reach the order of 10^{-3} at 800 nm by the excitation of 980 nm diode laser [12,13]. In addition, the sensitivity for the $^3F_{2,3}$ & $^3H_4$ energy level pair of Tm^{3+} is twice as high as that for the $^2H_{11/2}$ & $^4S_{3/2}$ energy level pair of Er^{3+} due to a larger energy gap [14]. Else, the $^3F_{2,3}$ level is strongly affected by non–thermal population, which results in the deviation of the temperature dependence of FIR from the pure Boltzmann law [14].

In this study, taking the $^3F_{2,3}$ & $^3H_4$ levels of Tm^{3+} as an example of a thermally coupled energy level pair, a correcting method for an upconversion populated system is presented and experimentally tested. First, the temporal evolutions of population from the pair are theoretical studied and a method of obtaining thermal population degree is presented; second, the time-resolved fluorescent spectra of these pairs at different temperatures were studied and corresponding η values were

* Corresponding authors.
E-mail addresses: qinfeng@hit.edu.cn (F. Qin), zhangzhiguo@hit.edu.cn (Z. Zhang), dzk@psu.edu (W. Cao).

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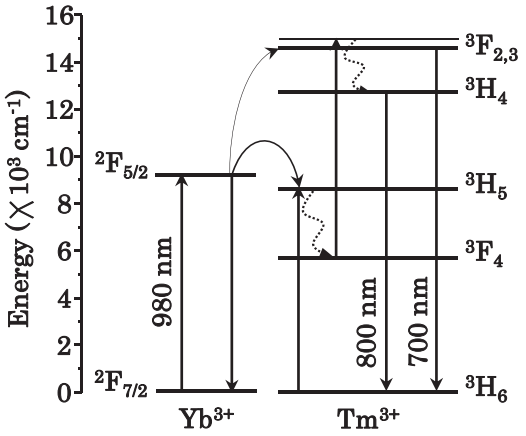

Fig. 1. The energy level diagram for Tm^{3+} and Yb^{3+} as well as the upconversion mechanisms.

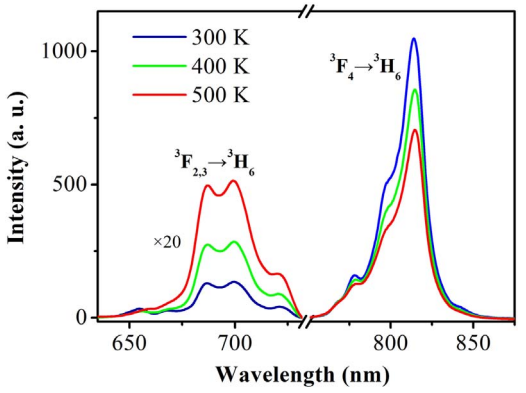

Fig. 2. Typical luminescence spectra of Tm^{3+} at various temperatures under the excitation of 980 nm diode laser.

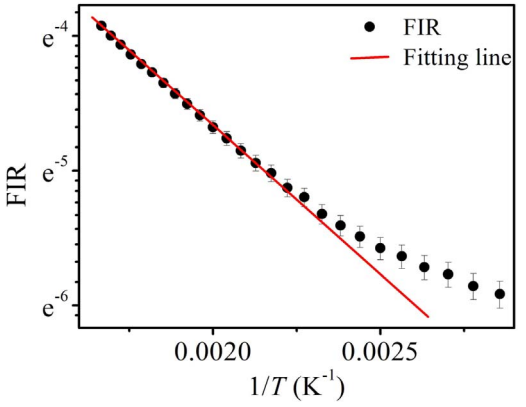

Fig. 3. Temperature dependence of FIR and fitting curves on a logarithmic scale.

obtained from the decay profiles; third, the correcting curves were presented and the correcting results were evaluated. In addition, some thermal coupling related physical problems are discussed at the end.

2. Theory and method

Generally, two successive energy transfer processes are needed in the population of the $^3F_{2,3}$ states of Tm^{3+}, which results in the near infrared emission around 700 nm. A subsequential nonradiative relaxation from the $^3F_{2,3}$ states populates the $^3H_4$ state, and the intense 800 nm near-infrared emission is then produced [14]. The energy level diagrams of Tm^{3+} and Yb^{3+} as well as corresponding transitions are illustrated in Fig. 1. For simplicity, the $^2F_{5/2}$ and $^2F_{7/2}$ levels of Yb^{3+} are labeled as 0' and 1'; the $^3H_6$, $^3F_4$, $^3H_4$ and $^3F_{2,3}$ levels of Tm^{3+} are labeled as 0, 1, 2 and 3, respectively.

For decay processes, there are no pumping terms. The differential equations guiding the dynamic processes of the concerned levels in Fig. 1 can be written as:

$$\frac{dn_{1'}}{dt} = -A_{1'}n_{1'}, \tag{2}$$

$$\frac{dn_1}{dt} = C_0 n_{1'} n_0 - C_1 n_{1'} n_1 - A_1 n_1, \tag{3}$$

$$\frac{dn_2}{dt} = C_1 n_{1'} n_1 - T_2 n_2 - A_2 n_2 - W_2 n_2, \tag{4}$$

$$\frac{dn_3}{dt} = T_2 n_2 - W_3 n_3 - A_3 n_3, \tag{5}$$

where n_i, A_i, C_i and W_i are the population, radiative transition probability, energy transfer rate and nonradiative relaxation probability of the state i, respectively; T_2 is the thermal population probability from level 2 ($^3H_4$ level) to level 3 ($^3F_{2,3}$ levels) [15]. Using the initial conditions $n_i(t=0)=n_{i0}$, the temporal evolution of the population in these emitting levels could be obtained from above equations:

$$n1'(t) = n_{0'}e^{-A_{1'}t}, \tag{6}$$

$$n_2(t) = \chi_0 e^{-A_{1'}t} + (n_{20} - \chi_0)e^{-(A_2+W_2+T_2)t}, \tag{7}$$

$$n_3(t) = \frac{\chi_1}{A_3+W_3}e^{-A_{1'}t} + \frac{\chi_2}{A_3+W_3}e^{-(A_2+W_2+T_2)t} + (n_{30} - \frac{\chi_1+\chi_2}{A_3+W_3})e^{-(A_3+W_3)t}, \tag{8}$$

with the parameters $\chi_0 = \frac{C_1 n_{10} n_{1'0}}{A_2+W_2+T_2-A_{1'}}$, $\chi_1 = \frac{(A_3+W_3)T_2\chi_0}{A_3+W_3-A_{1'}}$, $\chi_2 = \frac{(A_3+W_3)T_2(n_{20}-\chi_0)}{(A_3+W_3)-(A_2+W_2+T_2)}$, and $\chi_3 = n_{30}(A_3+W_3) - \chi_1 - \chi_2$.

According to Einstein's theory, the fluorescence intensity is proportional to the population of the energy level, or the depopulation rate. Therefore, the depopulation rate of the thermally coupled pair can be further deduced from Eqs. (7) and (8):

$$\frac{dn_2(t)}{dt} = -A_{1'}\chi_0 e^{-A_{1'}t} - (A_2+W_2+T_2)(n_{20}-\chi_0)e^{-(A_2+W_2+T_2)t}, \tag{9}$$

$$\frac{dn_3(t)}{dt} = -\frac{A_{1'}\chi_1}{A_3+W_3}e^{-A_{1'}t} - \frac{\chi_2(A_2+W_2+T_2)}{A_3+W_3}e^{-(A_2+W_2+T_2)t} - \chi_3 e^{-(A_3+W_3)t}. \tag{10}$$

For the temporal evolution of the population in level 2, a bi-exponential decay behavior was indicated. However, the energy transfer term from level 1' to level 1 illustrated in Eq. (4) cannot be found in Eq. (9). On the other hand, for the temporal evolution of the population in level 3, a tri-exponential decay behavior was demonstrated. However, the thermally populating term from level 2 to level 3 illustrated in Eq. (5) cannot be found in Eq. (10). To clarify the physical picture, the populating term is preserved and Eqs. (9) and (10) are accordingly rewritten as

$$\frac{dn_2(t)}{dt} = C_1 n_{10} n_{1'0} e^{-A_{1'}t} - (A_2+W_2+T_2)\chi_0 e^{-A_{1'}t} - (A_2+W_2+T_2)(n_{20} - \chi_0)e^{-(A_2+W_2+T_2)t}, \tag{11}$$

$$\frac{dn_3(t)}{dt} = T_2\left[\chi_0 e^{-A_{1'}t} + \left(n_{20}-\chi_0\right)e^{-(A_2+W_2+T_2)t}\right] - \chi_1 e^{-A_{1'}t} - \chi_2 e^{-(A_2+W_2+T_2)t} - \chi_3 e^{-(A_3+W_3)t}. \tag{12}$$

For Eq. (11), the first positive term is the preserved populating term, whereas the two negative terms denote the radiation from the lower level (level 2) to the ground state. For Eq. (12), the first positive term is the preserved thermal populating term, whereas the three negative terms denote the radiation from the upper level (level 2) to the ground state. Therefore, the measured fluorescence decay curves from a pair of