Theoretical modelling of photoluminescence from thermally coupled levels

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Introduction

Optical thermometry, being based on temperature (T) dependencies of optical properties of materials, is of a great engineering interest, as allows for contactless temperature monitoring in various fields. Fluorescence intensity ratio (FIR) is a technique discussed since 1970s and widely studied up to the present time. The technique is based on the analysis of two monitored emission lines and, respectively, requires a presence of two thermally coupled levels (TCLs) of luminescence. On the one hand, these levels should not be very distant in energy, which must provide enough variation of populations in the interested temperature range. Otherwise, TCLs cannot be very close located, as the respective spectral lines should be easy resolvable. A theory of TCL luminescence excited by an external sensitization is presented in this work and applied to the emission from excited levels $^2H_{11/2}$,$^4S_{3/2}$ to the ground one $^4I_{15/2}$ of Er^{3+} ions in AlN matrix.

Methods

AlN:Er^{3+} film was prepared on a sapphire (c-plane) substrate by radio frequency magnetron sputtering. An Al:Er alloy (99.9%) with the Er concentration of 2 at% was used as a target. The deposition pressure in a growth chamber was 0.3 Pa at 350 ºC. The gas atmosphere in the chamber was nitrogen (99.999%) and argon (99.999%), with the flow velocities of 10 SCCM and 20 SCCM, respectively. The sputtering time of the film was 20 min, and the power was 150 W.

PL spectra in the visible range were obtained with a spectral resolution of 0.337 nm using a Jiangsu Dowell PL/Raman confocal microscope system with a 50X objective attached to an Andor SR500 spectrometer equipped with a Newton 920 CCD detector. The NIR PL spectra were measured using a NIR-Quest Ocean Optics spectrometer with a spectral resolution of 1 nm. The PL was excited by a 532 nm laser at a power density of 1.7 mW/μm2.

Results and Discussion

The room-temperature PL spectrum of the AlN:Er^{3+} film has been measured under 532 nm excitation. In the visible range (Fig. 1a), two luminescence bunches of peaks at 540 and 560 nm are observed (a green emission). They are related to the transitions $^2H_{11/2}\rightarrow{}^4I_{15/2}$ and $^4S_{3/2}\rightarrow{}^4I_{15/2}$ in Er^{3+} ions. The origins of the rest of lines are indicated nearby. Fig. 1b shows all observed transitions of the Er-4f levels.

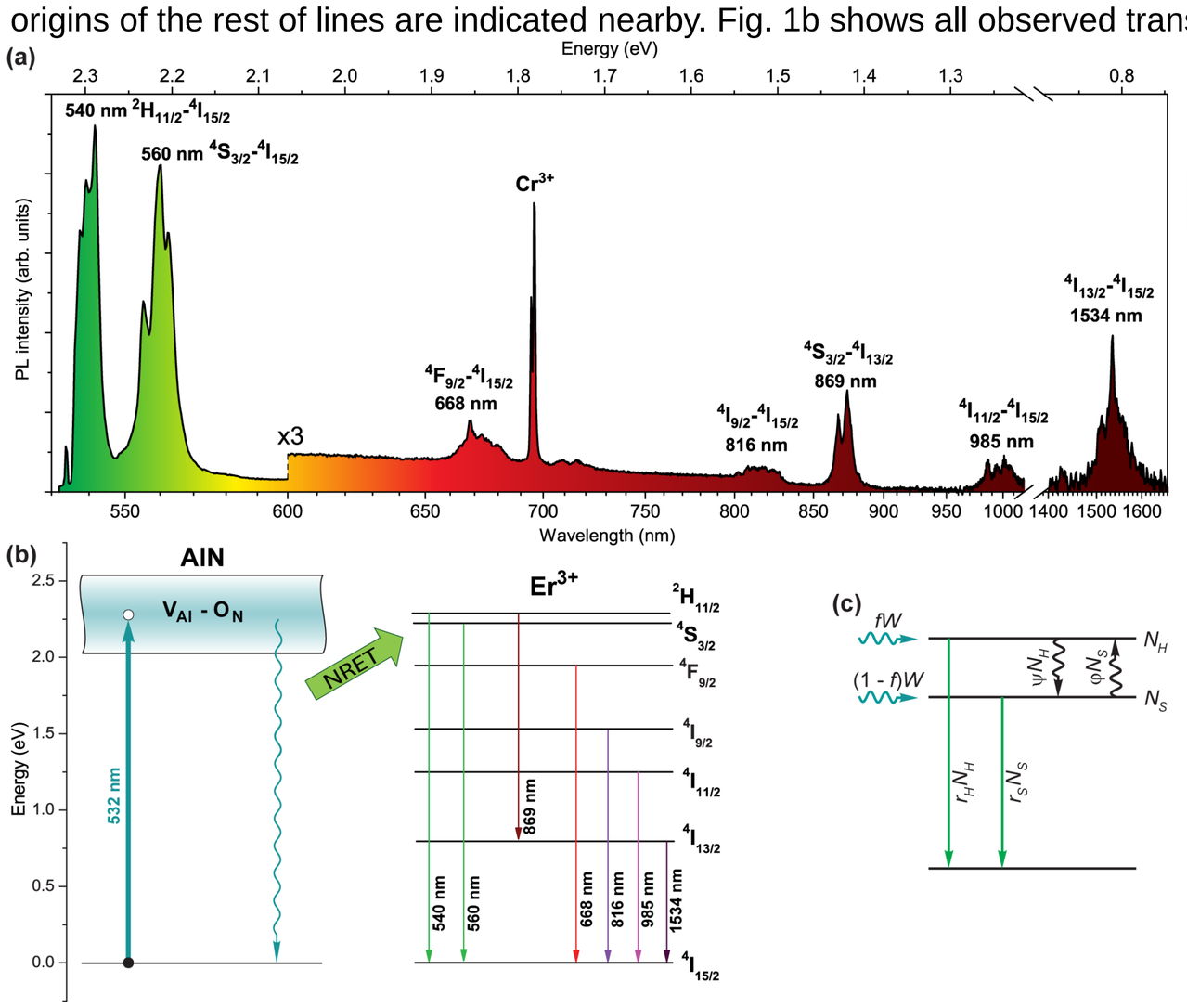

Fig. 1. (a) The room-temperature Vis-NIR PL spectra of the AlN:Er^{3+} film at 532 nm excitation. (b) The excitation pathway via the AlN-to-Er^{3+} energy transfer and the luminescence transitions in Er^{3+}. (c) The rates of the transitions involving two TCLs.

When rising *T*, the PL intensity at 560 nm decreases, while, on the contrary, that at 540 nm increases (Figure 2a). The latter *T*-behavior is atypical for PL and should be explained in detail.

Modelling

Dynamics of the concentrations of Er ions on the excited states $^2H_{11/2}$ and $^4S_{3/2}$, respectively, is

$$\frac{dN_H}{dt} = fW - r_HN_H - q_HN_H + q_SN_S \quad (1)$$

$$\frac{dN_S}{dt} = (1-f)W - r_SN_S - q_SN_S + q_HN_H \quad (2)$$

where *W* is the total rate of excitation of Er^{3+} to both $^4S_{3/2}$ and $^2H_{11/2}$, *f* is the fraction of the Er^{3+} centers being optically excited onto the level $^2H_{11/2}$, thus *fW* and (1 – *f*)*W* are the rates of excitation to the $^2H_{11/2}$ and $^4S_{3/2}$ levels, respectively. Parameters $r_{H,S}$ are the probabilities (reciprocal time constants) of the radiative transitions, ψ and φ are probabilities of the excitation exchange. The effect of temperature on the system manifests through the dependence $\varphi(T) = \varphi_\infty\cdot\exp(-\Delta\varepsilon/kT)$, where Δε is the energy distance between the TCLs and φ_∞ is the value for $T\rightarrow\infty$.

In the stationary mode, when $dN_H/dt = dN_S/dt = 0$, the luminescence intensity from the level $^4S_{3/2}$ reveals a usual dependence on temperature, following Mott formula, while that from $^2H_{11/2}$ is predicted to rise with *T*:

$$I_{540nm} \equiv I_H = r_HN_H = \frac{q_S+fr_S}{q_S+r_S(1+q_H/r_H)}W \quad (3)$$

$$I_{560nm} \equiv I_S = r_SN_S = \frac{r_S}{r_H}\cdot\frac{q_H+r_H(1-f)}{q_S+r_S(1+q_H/r_H)}W. \quad (4)$$

Basing on Eqs. (7) and (8), the FIR in Fig. 2b should follow an exponential function

$$FIR = \frac{I_{540nm}}{I_{560nm}} = \frac{q_S/r_S+f}{q_H/r_H+1-f} = \frac{\frac{q_{S\infty}}{r_S}\cdot\exp(-\Delta\varepsilon/k_BT)+f}{q_H/r_H+1-f} = A_0 + A_1\cdot\exp(-\Delta\varepsilon/k_BT) \quad (5)$$

where A_0 and A_1 are constants independent on *T*. Fitting the experimental dependence (red curve in Fig. 2b), we extracted more precisely the activation energy Δε = 76 meV, which is very close to that of ~79 meV obtained above when analyzing the PL band positions. Respectively, the characteristic *T* is $\Delta\varepsilon/k_B \approx 875$ K.

It is worth noting that a Boltzmann distribution of population is usually deemed for the excited levels, i.e., $A_0 = 0$ should be in Eq. (5). Nevertheless, according to the considered theory, it depends on the excitation way of Er^{3+} ions and is correct when $f = 0$ or, at least, $f << q_{S\infty}/r_S$. Anyway, the best fitting parameter $A_0 \approx 8.4\times10^{-2}$ in Fig. 3b is more than two orders less than $A_1 \approx 18.9$, thus a Boltzmann distribution is quite acceptable.

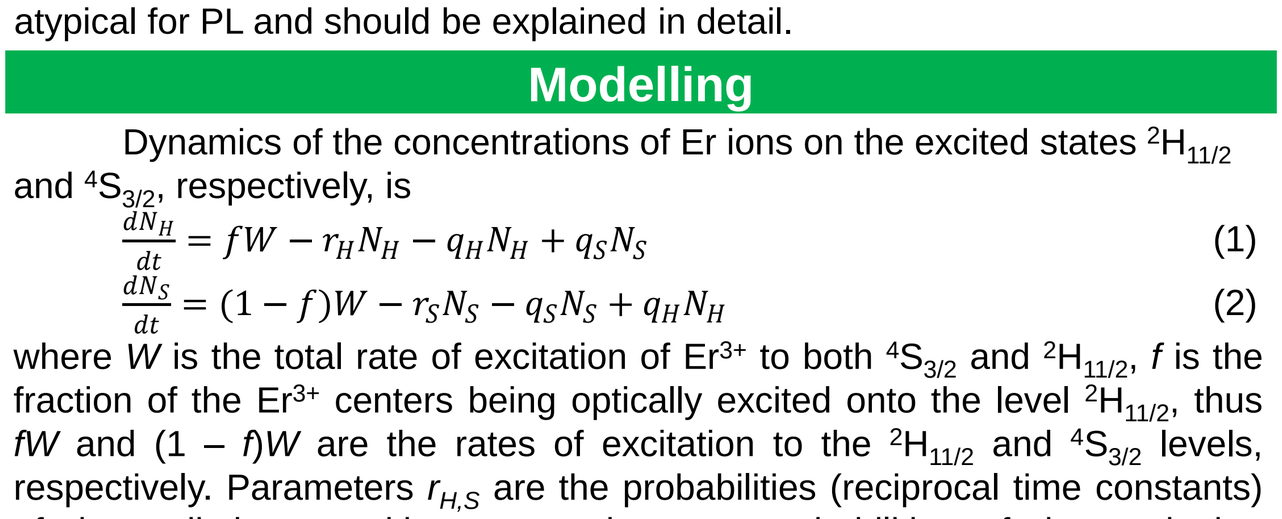

Fig. 2. (a) Temperature-dependent PL of the green spectrum range of the AlN:Er^{3+} film excited by 532 nm laser. (b) FIR of two green PL bands and its best fitting by function (5), as well as the 1st derivatives of both the experimental and fitting data as the absolute sensitivity.

Conclusions

Temperature-driven PL characteristics of the Er^{3+}-doped AlN film prepared by radio frequency magnetron sputtering have been studied within 110-550 K in terms of optical thermometry. It shows a quite bright PL in the visible (540, 560 and 668 nm) and NIR (816, 869, 985 and 1534) ranges. The PL at 560 nm ($^4S_{3/2}\rightarrow{}^4I_{15/2}$) shows a typical dependence of intensity on *T*, following Mott formula. Otherwise, the PL at 540 nm ($^2H_{11/2}\rightarrow{}^4I_{15/2}$) atypically increases with *T*. The increase is theoretically modelled when assuming a thermal transition between the excited states $^4S_{3/2}\rightarrow{}^2H_{11/2}$.

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