An inquiry into “Non-radiative processes” for development of truly valuable luminescent materials

NIMS, Surface Physics and Structure Unit (SPSU), Surface Physics Group
Masashi Ishii
ISHII.Masashi@nims.go.jp

1. Research purpose

I am not doubtful of the ability of optical measurements such as photoluminescence in evaluation of luminescent materials. However, the optical measurements observe a small minority, if enormous non-radiative processes hide in the materials. Although we are always attracted by a novel luminescence mechanism, the key to fabricate truly valuable materials should be identification and minimization of the non-radiative processes.

Obviously, it is inconsistent to analyze non-radiative processes using optical measurements. The purpose of this research is establishment of a quantitative analytical method of the non-radiative processes and its application to development of luminescent materials.

2. Electric response measurement of luminescent materials

In order to analyze the radiative and non-radiative processes equally, we adopt an electric measurement. Considering that the emission is induced by injected charges and that the non-radiative process is thermal loss and reflection of the injected charges, the electric measurement sensitive to the charges can cover the research purpose. Photocurrent response to a pulsed excitation light may be a typical example of the electric measurements. In this study, however, by using the mathematical equivalency between time- and frequency-responses through the Fourier transform, the processes are investigated with a spectroscopy. The advantages of the spectroscopy are as follows:

(1) Windowing key frequency band improves the accuracy of the measurement.
(2) Since non-radiative processes respond at a specific frequency, the spectra can be deconvolved and analyzed individually.
(3) From phase analysis of the frequency response, the origin of the non-radiative processes, such as thermal loss and reflection can be quantified.
(4) Anomalous behavior is possibly reflected in the spectral shape.

3. Analysis of the non-radiative processes

We have analyzed non-radiative processes in Si nano-crystals (Si-nc, Si-nc:P) and rare-earth doped semiconductors (TiO_2:Sm, Si-nc:Er, GaAs:Er).[1-4] The common procedure of the analyses is

(i) Measurement of current response spectra by applying AC electric field to photo-excited sample and scanning AC frequency,
(ii) Identification of the origin of the non-radiative processes using thermal quenching, and
(iii) Comparison between photo-excited and ground states to evaluate contributions of photon and intrinsic property of the materials.

From (i), an equivalent circuit (parallel connection of resistance R and capacitance C) that represents the spectrum can be deduced, and it quantifies the thermal loss and reflection in the non-radiative processes. For (ii), variation in R and C with respect to temperature clarifies the origin of the quenching.

Figure 1 shows electrically evaluated a thermal quenching process of luminescence for TiO_2:Sm. We confirmed that the response frequency ω_0 (that corresponds to a response time constant $\tau_0 = 1/\omega_0$ through the inverse Fourier transform) correlates with the quenching of Sm^{3+} luminescence, and proposed dynamics of non-radiative process from a spectral feature i.e., broadening spectrum with increasing temperature. The broadening can be explained by hopping charges in a sub-band of TiO_2.

Thus, the electric measurement can quantify the non-radiative processes. The result is expected to be used as a criterion for development truly valuable luminescent materials.

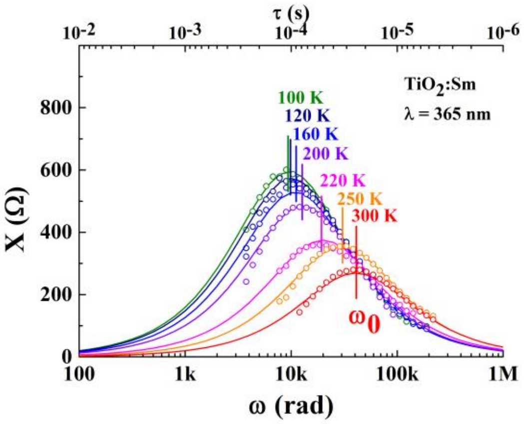

Fig. 1 Electrically evaluated thermal quenching of Sm^{3+} luminescence of TiO_2:Sm

References

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2) M. Ishii *et al*., Appl. Phys. Lett. 101, 242108 (2012).
3) M. Ishii *et al*., J. Appl. Phys. 111, 053514, (2012).
4) M. Ishii *et al*., Appl. Phys. Lett., 99, 101909 (2011).