Journal of Luminescence 188 (2017) 313–318

Contents lists available at ScienceDirect

Journal of Luminescence

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

Characteristic features of spectrally resolved luminescence in crystalline phosphors

Ewa Mandowska

Institute of Physics, Jan Długosz University, ul. Armii Krajowej 13/15, 42-200 Częstochowa, Poland

ARTICLE INFO

Keywords:
Thermoluminescence (TL)
Spectrally resolved thermoluminescence (SR-TL)
Optically stimulated luminescence (OSL)
Phosphorescence
Traps
Recombination centers

ABSTRACT

Wide gap crystalline phosphors are often used as luminescent solid state detectors in modern dosimetry of ionizing radiation. Typically, thermoluminescence (TL) and optically stimulated luminescence (OSL) phenomena are used for these purposes. This type of long lived luminescence is typically attributed to trapping and recombination of charge carriers at various defects of the solid. These defects are related to deep trap levels within the energy gap. Theoretical models predict localized, delocalized or semi-localized recombination route for the processes in various solids. The different routes may occur simultaneously during TL or OSL readout. Usually, it is difficult to distinguish these mechanisms. This paper presents some methods that allow to identify delocalized transitions from spectrally resolved TL, OSL and phosphorescence measurements. The methods were tested numerically to prove their applicability in typical cases.

1. Introduction

Luminescent solid state detectors are now a standard in modern dosimetry of ionizing radiation. Typically, the detectors are crystalline wide band gap dielectric phosphors exhibiting extremely long-lived luminescence. The luminescence could be observed in the form of thermoluminescence (TL), optically stimulated luminescence (OSL) or isothermal phosphorescence (Ph). TL and OSL phenomena are extensively used also for archaeological/ geological dating (for review see [1]). TL could be observed when a sample is excited at appropriately low temperature T_0 by a high-energy radiation (e.g. UV or X-rays). Then, the excitation is removed and the sample is heated, usually with a constant rate β, i.e. $T(t) = T_0 + \beta t$. During heating, luminescence emitted by the sample is measured. A special case of TL is an isothermal decay, which we call phosphorescence. In OSL measurements the stimulating factor is light. In most applications the OSL emission is observed at shorter wavelengths than the stimulation wavelength.

In most cases the luminescence is very week so it is measured mostly by photon counting technique using low background bialkaline photomultipliers. This ensures high sensitivity but the information on spectral properties is lost. Nevertheless, spectral measurements are possible when a phosphor is excited with a higher dose. Therefore, so-called spectrally resolved thermoluminescence (SR-TL) could provide additional information regarding the distribution of recombination centers related to the luminescence. These measurements require advanced experimental setup [2,3] and special methods of data handling [4,5].

With all the range of applications, still the physical basis involved in the kinetic mechanisms of the processes is not well known. This type of long-lived luminescence occurs only in high energy band gap dielectric solids. Therefore, the processes are attributed to trapping and recombination of charge carriers at various defects of the solid, which are related to deep trap levels within the energy gap.

Theoretical models predict delocalized, localized or semi-localized (i.e. mixed) recombination route for the processes in various solids. Historically, first models assumed random distribution of localized trap and recombination center (RCs) levels with delocalized transition of charge carriers. These levels have the capability of capturing electrons and holes, respectively. For the model with active electron traps the process of releasing electrons (detrapping) goes through conduction band. Therefore, the target RC is not directly related to the trap where the electron comes from. The simplest case of the delocalized model was considered by Randall and Wilkins [6]. The more complex delocalized model is known as the simple trap model (STM) [1,7]. Another extreme case is the model of localized transitions (LT) by Halperin and Braner [8] regarding hole-electron pairs trapped close to each other. The model was later modified by Land [9]. In the LT model detrapping and recombination occur locally within the hole-electron pair. It was shown that 'localized' TL glow curves obey always first order kinetics [1,10].

Although, the models involving many traps and RCs are mathematically complex, they do not provide convincing explanations with respect to many features frequently found in TL and OSL detectors. Mandowski [11] proposed a more general model of semi-localized

E-mail address: e.mandowska@ajd.czest.pl.

http://dx.doi.org/10.1016/j.jlumin.2017.04.053
Received 6 April 2017; Received in revised form 21 April 2017; Accepted 25 April 2017
Available online 26 April 2017

transitions (SLT). The model includes both STM and LT properties [11,12] as well as predicts some new effects [13]. Other possibilities relate to simultaneous participation of electrons and holes (two carrier kinetics – [14,15]) or complex cluster models [12,16,17].

In real phosphors the different recombination routes – delocalized, localized or semi-localized – may occur simultaneously during TL, OSL as well as typical isothermal phosphorescence decay measurements. Usually, it is difficult to distinguish these mechanisms. This paper presents some methods that allow identifying delocalized (and in some cases localized) transitions from spectrally resolved measurements. This information is of great importance for the analysis and interpretation of long lasting luminescence. In the case of negative verification the particular emission band could be attributed to other mechanisms including semi-localized, cluster or two-carrier models. Range of possible applications is very broad. To show the usefulness of these methods numerical calculations were carried out using a complex model consisting of several traps and recombination centers with mixed localized and delocalized transitions.

2. Theory

2.1. Delocalized mechanism of recombination

The extended STM model consists of many discrete electron traps and RCs within the energy gap. The relevant energy diagram is shown in Fig. 1. After excitation some of the traps and RCs are filled with electrons and holes, respectively. Optical or thermal stimulation releases the electrons to the conduction band. Free electrons could be retrapped or recombine with holes in RCs producing luminescence. The relevant set of kinetic equations for this case is the following:

$$-\dot{n}_i = n_i P_i - n_c A (N_i - n_i), \qquad i = 1..p \tag{1a}$$

$$-\dot{h}_j = B_j h_j n_c, \qquad j = 1..q \tag{1b}$$

$$\sum_{j=1}^{q} h_j = \sum_{i=1}^{p} n_i + n_c + M, \tag{1c}$$

The probability density of charge carriers detrapping from i-th trap level P_i may relate to thermal or optical stimulation. Therefore the relevant equation for this coefficient is given by

$$P_i(t) = \nu_i \exp\left(\frac{-E_i}{kT(t)}\right) + \Phi(t)\sigma_i \tag{2}$$

In the above equations, the subscripts i and j number trap levels and RCs respectively. E_i stand for the activation energy, N_i, n_i and h_j denote the concentrations of trap states, electrons trapped in 'active' traps and holes trapped in RCs, respectively. Dots over variables denote, as usual, time t derivatives. M stands for the number of electrons in so-called thermally disconnected traps (deep traps). These traps do not participate directly in charge carrier transport and luminescence processes but rather they constitute a reservoir of charge carriers. A and B coefficients stand for the trapping and recombination probability densities, respectively, ν is the frequency factor and k is the Boltzmann constant. For optical stimulation Φ denotes the intensity of stimulating light and σ_i denotes the relevant optical cross section for the i-th trap level. The set of equations (1) has no analytical solutions in general case.

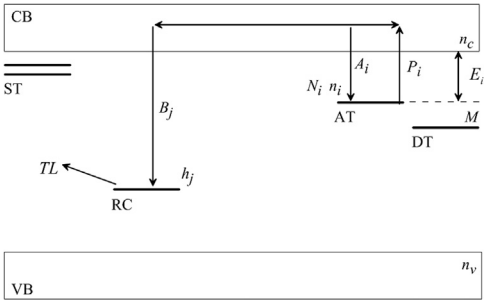

Fig. 1. Energy diagram for the extended simple trap model (STM) involving delocalized transitions. CD – conduction band, VB – valence band, ST – shallow traps, AT – active traps, DT – deep traps, RC – recombination centers. For the i-th trap level: E_i – activation energy, P_i – stimulating function (Eq. (2)), A_i – retrapping coefficient, N_i – concentration of traps, n_i - concentration of electrons. For the j-th recombination center: B_j – recombination coefficient, h_j – concentration of holes. n_c – concentration of electrons in the conduction band, n_v – concentration of holes in the valence band.

In a long lived luminescence several RCs may be active concurrently. Each of them contributes to the total luminescence at specific (presumably different) range of wavelengths. Using apparatus for spectrally resolved measurements (e.g. a CCD camera with a spectrograph [2,3]) one is able to determine various emission bands relating to different types of RCs. Therefore, for each RC we define

$$\mathcal{L}_j(t) = -c_j \dot{h}_j(t) \tag{3}$$

where c_j is a proportionality coefficient dependent on measurement conditions. Experimentally, $\mathcal{L}_j(t)$ could be determined by integrating luminescence intensity over the whole emission band.

Analyzing spectrally resolved measurement, i.e. a measurement where each spectral component is recorded separately, it is easy to obtain temporal dependence of each RC solving Eq. (1b):

$$h_j(t) = h_{j0} \exp\left(-B_j \int_0^t n_c(t')dt'\right) \tag{4}$$

For convenience we will denote

$$\vartheta(t) = \int_0^t n_c\,(t')\,dt' \tag{5}$$

Hence the intensity of luminescence coming from each RC according to Eq. (3) is given by

$$\mathcal{L}_j(t) = c_j h_{j0} B_j n_c\,(t) \exp\,(-B_j \vartheta(t)) \tag{6}$$

An additional, easy measurable quantity is the integral:

$$S_j(t) = \int_0^t \mathcal{L}_j(t')dt' = c_j h_{j0}[1 - \exp(-B_j \vartheta(t))] \tag{7}$$

2.2. Localized mechanism of recombination

The localized transition (LT) model was considered by Halperin and Braner [8]. They assumed that traps and RCs are closely correlated in space forming pairs that can be considered as independent units - i.e. all charge transfer takes place within groups of one kind, each having one trapping state, one excited state and one RC. The model is schematically depicted in Fig. 2. Correct equations for this case were given by Land [9]:

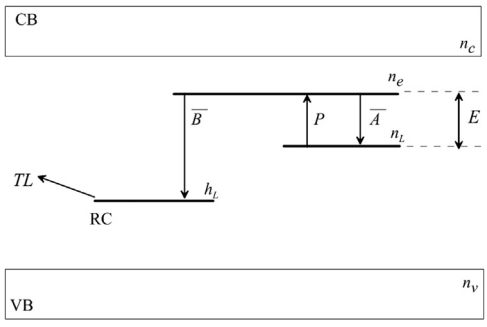

Fig. 2. Energy diagram for the localized transitions model (LT). CD – conduction band, VB – valence band, RC – recombination centers. E – activation energy, P – stimulating function (Eq. (2)), $\overline{A}$ – retrapping coefficient, $\overline{B}$ – recombination coefficient, n_L - concentration of electrons in traps, n_e - concentration of electrons at the excited level, h_L – concentration of holes, n_c – concentration of electrons in the conduction band, n_v – concentration of holes in the valence band.