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Duplicitous thermoluminescence peak associated with a thermal release of electrons and holes from trapping states

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Abstract

A thermoluminescence (TL) glow peak may result from a transition of electrons from traps into the conduction band, followed by a recombination with holes trapped in a luminescence center. Another possibility is that holes trapped in a hole trap are thermally released into the valence band and recombine with electrons in an electron recombination center. A series of glow peaks emitted from a given sample may include peaks of both kinds. In some cases, peaks may be identified as being of one kind or the other, say, by using thermally stimulated electron emission (TSEE), which can take place when the free carriers are electrons. In the present work, we demonstrate by the use of simulation that two peaks may result from one electron and one hole trapping states and a single hole recombination center. The first TL peak is observed when thermally stimulated electrons recombine with holes in the center. The TL peak is terminated when the holes in the center are exhausted. At higher temperatures, holes from a hole trap are released into the valence band and then captured by the hole center, thus this center is replenished. More electrons from the electron trap are thermally released now and recombine with the newly arrived holes in centers. A second TL peak may be observed which carries some information concerning the hole trap. It is thus demonstrated that some of the usual methods for distinguishing between electron and hole traps can lead to incorrect conclusions. It is possible for a hole trap, for example, to induce an increase in electron recombination in such a way that it produces a peak that looks nearly identical to TL from an electron trap. This simulation may bring about a new look at TL peaks occurring in materials used in TL dosimetry and dating. A new interpretation may also be given to "Auger" TSEE associated with the thermal release of electrons from the surface of a material, which indirectly results from the thermal release of holes from traps. The performance of some methods for evaluating the activation energies and the significance of the results in the present situation are discussed.
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1. Introduction

Thermoluminescence (TL) glow curves usually consist of a number of peaks occurring at different temperatures. The accepted theory of TL considers charge carriers, which during excitation are captured in traps, and luminescence centers within the forbidden gap of the material being used. The model may include either electron traps and hole centers or hole traps and electron centers. In the former case, during the heating stage, electrons are thermally raised into the conduction band and

recombine with holes in luminescence centers, yielding an emission of luminescence. In the latter, holes are thermally released from traps into the valence band and recombine with electrons in luminescence centers yielding the emission of TL. It has been shown that both kinds of peaks may take place in the same material. Thus, a thermoluminescent material may yield separate sets of peaks, one due to thermally released electrons recombining with stationary holes in centers and another set due to thermally released holes recombining with electrons in other luminescence centers (see e.g. Braner and Israeli, 1963). Different TL peaks in a given material may yield different emission spectra due to the radiative recombinations in different recombination centers. The work by Braner and Israeli (1963)

distinguishes between electron and hole processes in each of four alkali halides, KBr, KI, NaCl and KCl. It has later been shown by McKeever et al. (1985) that electrons and holes may be released simultaneously from their trapping states. The electron trapping states may be considered at the same time as electron traps and electron luminescence centers and the hole trapping states as hole traps and hole luminescence centers. Under these circumstances, the observed TL may be the sum of two radiative transitions, namely free electron to bound hole and free hole to bound electron. More aspects of this rather complex process can be considered. For example, holes may be thermally released from a hole center, thus reducing the expected amount of luminescence from the center in question. Inversely, a hole trap may thermally release holes into the valence band, which can be captured in an active luminescence center, thus changing the subsequently measured luminescence from this center. This was the way sensitization of the 110 °C peak in quartz was explained by Zimmerman (1971). Additional possibilities are implied in the work by Bailey (2001) who studied in depth the TL as well as the optically stimulated luminescence (OSL) in quartz, material that is broadly used for luminescence dating of archaeological and geological samples. His model includes five electron-trapping states and four hole levels. Depending on the relevant trapping parameters, electrons and holes may be released into the respective bands, and may recombine with opposite charge carriers in centers. The emitted luminescence, TL or OSL, is associated here with only one transition of free electrons with holes in centers. The resulting TL glow curve simulated by Bailey (2001) consists of a number of peaks associated with electrons released from different electron traps and recombining with holes in one of the centers. The experimental justification for this is that in quartz, the different TL peaks have the same emission spectrum. The role of the other centers in the model is their being competitors which can capture free electrons. Also, the free holes may be captured by the active luminescence center, thus replenishing it with holes, which may contribute to the TL occurring at a higher temperature.

Another, related, thermally stimulated phenomenon is thermally stimulated electron emission (TSEE). Here, thermally released electrons from the conduction band may be released from the surface of the sample and the resulting current may be measured as TSEE peaks as a function of temperature. Obviously, only electrons can be released from the surface, and therefore, TSEE has been used to distinguish between electron and hole transitions. However, an "Auger" TSEE was also reported in different materials. Here, somewhat anomalously, transitions, which are identified as being associated with the release of holes, may produce a measurable TSEE peak. As explained by Tolpygo et al. (1966) and Bindi et al. (1997), the Auger-like model involves the recombination of an electron and a hole. The energy released when an electron and a hole recombine may be transferred to another electron, localized in a nearby trapping state, which may thus acquire sufficient energy to overcome the potential barrier at the surface and be detected as an exoelectron.

In the present work, we focus on a situation in which in the temperature range of interest, electrons and holes are thermally released from their respective traps, whereas the radiative transition is assumed to be associated only with the recombination of electrons with holes in luminescence centers. The contribution of the hole trap is that it replenishes the hole center during the heating stage. As a result, one may see a duplicitous TL peak, the two components of which have the same emission spectrum since they are related to the same transition. The behavior of the free electron and free hole curves as a function of temperature are also followed; a new way is offered for explaining a TSEE peak associated primarily with the thermal release of trapped holes.

2. The model

The suggested model is shown in Fig. 1. This includes one electron trapping state, N_1, one hole trapping state, N_2 and one hole recombination center, N_3. This is the simplest model that enables the demonstration of the "duplicitous" peak, which results from the release of electrons and holes from trapping states, with recombinations in one center. During excitation, the applied radiation raises electrons from the valence band into the conduction band. The free holes may get trapped at the hole trap N_2 or at the hole center N_3. At the same time, the free electron can be trapped in the electron trap N_1 or recombine with a hole in the center, provided it has trapped a hole at an earlier stage of the excitation. The assumption that N_3 first captures a hole, which only then can recombine with a free electron, defines it as being a "hole center".

The set of simultaneous differential equations governing the process during excitation is

$$\frac{dn_1}{dt} = A_1(N_1 - n_1)n_c - n_1 s_1 \exp(-E_1/kT), \qquad (1)$$

$$\frac{dn_2}{dt} = A_2(N_2 - n_2)n_v - n_2 s_2 \exp(-E_2/kT), \qquad (2)$$

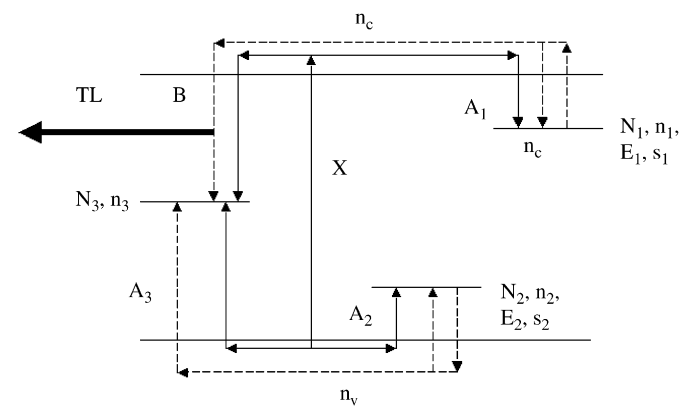$$\frac{dn_3}{dt} = A_3(N_3 - n_3)n_v - Bn_3 n_c, \qquad (3)$$

Fig. 1. The energy level diagram of one electron and one hole trapping states, and one kind of recombination center. Solid lines give transitions occurring during excitation and transitions taking place during read-out are shown by dashed lines. The TL emission is shown, schematically, by a thick arrow.

$$\frac{dn_c}{dt} = X + n_1 s_1 \exp(-E_1/kT) - A_1(N_1 - n_1)n_c - Bn_3 n_c, \qquad (4)$$

$$\frac{dn_v}{dt} = \frac{dn_1}{dt} + \frac{dn_c}{dt} - \frac{dn_2}{dt} - \frac{dn_3}{dt}. \qquad (5)$$

Here, N_1 (cm^{-3}) and n_1 (cm^{-3}) denote, respectively, the concentration and occupancy of electron traps, N_2 (cm^{-3}) and n_2 (cm^{-3}) the concentration and occupancy of hole traps and N_3 (cm^{-3}) and n_3 (cm^{-3}) the concentration and occupancy of hole centers, respectively. n_c (cm^{-3}) is the instantaneous concentration of free electrons and n_v (cm^{-3}) the concentration of free holes. X (cm^{-3} s^{-1}) is the rate of production of electron–hole pairs by the applied radiation, proportional to the dose-rate being used. A_1 (cm^3 s^{-1}) is the trapping probability coefficient of free electrons from the conduction band and A_2 (cm^3 s^{-1}) the trapping probability coefficient of free holes from the valence band into N_2. A_3 (cm^3 s^{-1}) is the probability coefficient for free holes from the valence band to recombine into the luminescence center and B (cm^3 s^{-1}) the probability coefficient of free electrons recombining with holes in the center. The relevant parameters for the thermal release of electrons is the activation energy E_1 (eV) and the frequency factor s_1 (s^{-1}), and for the release of holes, the activation energy E_2 (eV) and the frequency factor s_2 (s^{-1}); T (K) is the temperature and k (eV K^{-1}) is the Boltzmann constant.

The set of Eqs. (1)–(5) is solved numerically for a given set of the mentioned parameters and for the relevant value of X. Note that if the excitation takes place at relatively low temperatures, the terms exponential with the negative inverse temperature are negligible. If we denote the time of excitation by t_D, $D = X \cdot t_D$ is the total concentration per unit volume of electrons and holes produced, which is proportional to the total dose imparted. In order to simulate the experimental situation properly, one has to consider a relaxation time following the excitation and prior to the heating stage, during which practically all the free carriers relax and end up in the traps and centers. We therefore take the final values of the five relevant concentrations as initial values for the next stage of relaxation, set $X = 0$ and solve the equations for such a period of time that at the end both n_c and n_v are negligibly small.

The next stage is that of heating. Here, the same set of five simultaneous differential equations governing the process is solved. X is now set to zero and the terms including the temperature T become important at higher temperatures. We have to consider the heating function $T(t)$, and we take for simplicity a linear heating function, namely $T = T_0 + \beta t$, where β (K s^{-1}) is the constant heating rate. The emitted TL light, shown in Fig. 1 as the thick arrow, is associated with the recombination of free electrons with holes in the recombination center; this is given by

$$I(T) = Bn_3 n_c. \qquad (6)$$

3. Numerical results

The matlab odes23 solver was used to solve numerically the relevant sets of equations, as well as the Mathematica solver;
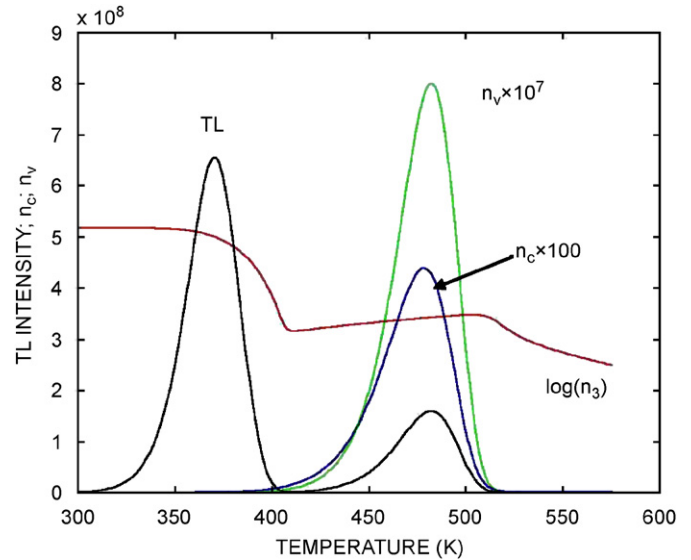

Fig. 2. For the set of parameters given in the text, the black line shows the two peaks of the simulated TL curve. The blue line depicts the free electron concentration and the green line, the free hole concentration. The red line represents the logarithm of the recombination center concentration $n_3(T)$.

the results reached by these parallel ways were in excellent agreement. Eqs. (1)–(5) were first solved for a certain value of the dose-rate X and for a certain length of the excitation time t_D, which together determine the dose $D = X \cdot t_D$. The solution of the same set of equations, but with $X = 0$, is continued for a further period of relaxation time. Finally, the coupled equations were solved for the heating stage, and Eq. (6) gave the TL intensity as a function of temperature. Fig. 2 shows the duplicitous TL peak simulated using the following set of parameters. $N_1 = 10^{12}$ cm^{-3}, $N_2 = 10^{13}$ cm^{-3}, $N_3 = 10^{14}$ cm^{-3}, $A_1 = 10^{-7}$ cm^3 s^{-1}, $A_2 = 3 \times 10^{-8}$ cm^3 s^{-1}, $A_3 = 2 \times 10^{-8}$ cm^3 s^{-1}, $B = 5 \times 10^{-6}$ cm^3 s^{-1}, $X = 5 \times 10^7$ cm^{-3} s^{-1}, $t_D = 1000$ s, $E_1 = 1.0$ eV, $E_2 = 1.3$ eV, $s_1 = 5 \times 10^{12}$ s^{-1}, $s_2 = 3 \times 10^{12}$ s^{-1}, $\beta = 1$ K s^{-1}. The black line depicts the simulated TL curve, with two peaks at ~ 370 and ~ 480 K. The $n_c(T)$ curve is shown by the blue line, with a single maximum occurring somewhat below the higher temperature TL peak. In order to be able to show the n_c curve on the same graph, the values have been multiplied by 100. The green line shows the $n_v(T)$ multiplied by 10^7, which also yields a maximum at ~ 480 K. The dependence of the hole concentration n_3 on temperature is also of interest. Since it varies by nearly 3 orders of magnitude in the temperature range of interest, it is shown on a semi-logarithmic scale as the red line. In order to be able to show it on the same scale as the other curves in Fig. 2, the values of $\log_{10}(n_3(T))$ have been multiplied by 5×10^7. This concentration of the center is seen to decrease up to > 400 K, then to increase slowly up to > 500 K when $n_3(T)$ is replenished, and then reduce further.

The occurrence of the high temperature TL and the $n_c(T)$ and $n_v(T)$ peaks at about the same temperature is somewhat surprising. In order to check whether this is merely a coincidence, we increased E_2 to higher values, keeping all other parameters constant, expecting that the $n_v(T)$ peak will shift

Table 1
Comparison of activation energies (eV) evaluated by the three methods

	Initial rise	Shape method	Various heating rate
1st TL peak	0.99	1.033	1.004
2nd TL peak	1.29	1.298	1.337
$n_c(T)$	0.98	1.06	1.296
$n_v(T)$	1.29	1.298	1.337

to higher temperature. This, indeed, happened, but at the same time the two other peaks shifted by about the same amount. This point along with an analytical explanation will be elaborated upon elsewhere.

Another point of interest is the evaluation of the activation energies and frequency factors using different methods. Obviously, the present situation is significantly more complicated than the traditional first-order, second-order or general-order cases. It is of interest, however, to follow the determined values of these parameters reached by the different methods, and in particular, to understand what features of the original different trapping states are thus evaluated.

In the initial-rise method, one plots $\ln(I)$ vs. $(1/T)$ in the initial-rise range, which quite arbitrarily is set here to be up to $\sim 5\%$ of the maximum intensity. The initial-rise activation energy is found using the slope of the straight line obtained, $E_{ir} = -k * \text{slope}$, where k is Boltzmann's constant. The values we received for the mentioned set of parameters were $E_{TL1} = 0.99\,\text{eV}$; $E_{TL2} = 1.29\,\text{eV}$; $E_{nc} = 0.98\,\text{eV}$ and $E_{nv} = 1.29\,\text{eV}$. Obviously, for the initial-rise results, the first TL peak as well as the free electron peak assumed quite accurately the activation energy of the electron trapping state, taken for the simulation as $1.0\,\text{eV}$. The activation energy for the second TL peak and the peak of concentration of free holes came out to be $1.29\,\text{eV}$, which is very close to the activation energy of the release of holes from the hole trap ($1.3\,\text{eV}$).

Another method used for evaluating the activation energy is the shape method. Since the peaks obtained did not behave like pure first- or second-order peaks, the heuristic general-order method has been utilized. For that, the shape factor $\mu_g = \delta/\omega$ has been evaluated, where $\delta = T_2 - T_m$ and $\omega = T_2 - T_1$, and where T_m is the temperature at the maximum, and T_1 and T_2 are, respectively, the low and high temperatures where the intensity reaches half maximum. Values of $\mu_g \cong 0.42$ and 0.52 are known to characterize first- and second- order peaks, respectively. The equation for evaluating the activation energy for these, as well as intermediate cases, is (Chen and McKeever, 1997, p. 114)

$$E = [2.52 + 10.2(\mu_g - 0.42)]\frac{kT_m^2}{\omega} - 2kT_m. \quad (7)$$

Yet another popular way for evaluating the activation energy is the method of various heating rates. In its simplest version, the sample is heated at two heating rates, β_1 and β_2, and the temperatures at the maximum, T_{m1} and T_{m2} are evaluated. The equation used (see e.g. Chen and McKeever, 1997, p. 122) is

$$E = k\frac{T_{m1}T_{m2}}{T_{m1} - T_{m2}} \ln\left(\frac{\beta_1 T_{m2}^2}{\beta_2 T_{m1}^2}\right). \quad (8)$$

Table 1 gives a comparison of the results attained by the mentioned three methods; these are discussed below.

4. Discussion

As pointed out above, the fact that the high temperature TL peak, the $n_c(T)$ and the $n_v(T)$ peaks occur at nearly the same temperature is somewhat surprising. It has been mentioned above, however, that while increasing the value of E_2, keeping all other parameters the same, not only the $n_v(T)$ peak shifts to higher temperature but also the $n_c(T)$ and TL peaks shift by about the same amount. A qualitative explanation to the fact that $I(T)$, $n_c(T)$ and $n_v(T)$ almost coincide in the relevant range will be given elsewhere. It should be noted that an important element of the occurrence of the duplicitous peak is the sizeable retrapping. In the temperature range between the two peaks, the probability per second of a thermally stimulated electron to retrap is larger than to recombine since the number of available holes in centers is small.

The evaluated activation energies as given in Table 1 are of interest. The fact that the first TL peak yields $0.99\,\text{eV}$ with the initial-rise method and $1.004\,\text{eV}$ with the VHR method agrees with its association with the release of electrons from traps $1.0\,\text{eV}$ deep. The effective value of $1.033\,\text{eV}$ found with the shape method is not too surprising in particular since the shape factor of the first TL peak is $\mu_g \approx 0.46$. The second TL peak, however, yields values of $\sim 1.3\,\text{eV}$ using all three methods, which shows that although the recombinations are of free electrons with holes in centers, the governing process here is the thermal release of holes and their trapping in recombination centers. The $n_v(T)$ curve yields consistently $E \cong 1.3\,\text{eV}$. The $n_c(T)$, however, yields $E_{IR} \approx 1.0\,\text{eV}$ with the initial-rise method which, indeed, is a feature of the release of electrons. However, when the VHR method is used, a value of $E_{VHR} \approx 1.3\,\text{eV}$ is obtained, which is a feature of the hole trap. The shape method yields here a value of $1.06\,\text{eV}$, which, apparently, has to do with the rather complex nature of the process under these circumstances. An important conclusion of the given results is that one should be rather cautious in ascribing specific transitions to the evaluated parameters when there is a possibility of having during the heating transitions of the described nature.

As for the Auger effect in TSEE, the explanation so far has been that a hole is thermally released into the valence band, recombines with an electron in a center and the energy released kicks out an electron into the conduction band, which can then be released from the surface of the sample. The present alternative is that the released holes ($n_v(T)$) indirectly induce a peak to form in the concentration of free electrons ($n_c(T)$), which may contribute to the TSEE.

We do not claim that the behavior reported here is general. It is suggested, however, that there is a possibility that should be considered that some TL peaks, which appear to be associated with the release of holes from hole traps, are actually associated with the recombination of free electrons and holes in recombination centers. The same explanation may apply to the occurrence of TSEE peaks, which carry features related to the release of holes from traps.

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