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Simultaneous determination of trap depth and the ratio of the rate of recombination to that of capture from thermo-luminescence*

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Thermo-luminescence (TL) is a kind of luminescence decay measured with varying temperature. In the process of TL the decay parameter itself involves the temperature effect of traps. Thus the trap depth is inseparable from the decay parameter. There are two separate peaks in the TL curve of ZnS:Cu,Co if the measurement starts from liquid nitrogen temperature. In the experiment we started from zero Celsius temperature to isolate the deeper traps. We have proposed and realized three methods for simultaneous determination of trap depth and decay parameter based on the quasi-equilibrium model and experimental data. If we treat the case of kinetic order $\alpha = 1$ as $\alpha = 2$, the error might be as large as 100%.

Keywords: thermo-luminescence, trap depth, monomolecular and bimolecular processes
PACC: 7860K, 7220J

1. Introduction

Trap is an important component in luminescent materials. Trap depth is its most important characteristic. It influences profoundly the character of luminance, e.g., when the intensity of photo-excitation changes from one value to the other, the corresponding change of luminescence intensity does not follow it at once. There appears a relaxation time. This relaxation is very sensitive to the temperature of the phosphor. Ordinarily, the luminescence belongs to recombination luminescence in which the electrons of the luminescent centres are excited to conduction band and they may return to the ionized luminescent centres or may be captured by localized traps. Only a part of the conduction electrons recombine with the luminescent centres and lead to emission. When electrons are released from the traps, they repeat again the processes of recombination and being trapped. Localized traps play a very important role in luminescence and the depth of them is the principal parameter.

Why are the simultaneous determinations of trap depth and the ratio of the rate of recombination to that of capture from glow curve necessary?

In the past, the luminescence decay was studied at first in the realm of classical physics. It was classified into two kinds. If the decay curve obeyed $\mathrm{d}n/\mathrm{d}t \propto -n$, it was called monomolecular (MM) process or first-order kinetics. If the decay curve obeyed $\mathrm{d}n/\mathrm{d}t \propto -n^2$, it was called bimolecular (BM) process or 2nd-order kinetics, where the light intensity $B = -\mathrm{d}n/\mathrm{d}t$. In most cases the decay does not obey either 1st or 2nd order kinetics and behaves in a more complicated manner. People cannot give a clear and reasonable explanation but assign the process with an arbitrary kinetic order $b(1 < b < 2)$. In 1947, Adirovich[1] proposed a quasi-equilibrium model based on energy band theory. The whole process of decay may be traced by the variation of the ratio of the rate of recombination with holes to that of capture

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by traps for conduction band electrons. The picture of the process is clear and the parameter characterizing decay curve has a definite physical meaning.

If in the process of decay the trapped electrons are released not at a constant temperature but with increasing temperature, the decay curve is termed glow curve. In other words, the glow curve of thermoluminescence (TL) is in fact a decay curve versus temperature. In the case of the decay curve (at a constant temperature) each point is determined by the temporal rate of the ratio of recombination to capture. However, in the case of the glow curve each point is determined not only by the temporal rate of the ratio of recombination to capture, but also by the temporal rate of electron release from the trap. They are not separable but closely interrelated with each other and in fact they are tangled into a single collective. Due to these effects, we should determine the relative rate of recombination versus capture (RRRC) for the decay curve. We determine it only simultaneously with the determination of trap depth. This is an inevitable situation in the analysis of simple glow curve.

Trap is a very important phenomenon in semiconductor. In luminescence traps may change the character of radiation especially in afterglow, and the trap depth is the principal parameter of a trap. There are several methods to estimate this depth, e.g, the absorption method, photo-capacitance method and the TL method. Among them the TL method is a relatively simple, perceptible and effective tool. In 1945–46 Randall and Wilkins[2] considered the development of TL as a mono-molecular (MM) process. But Antonov and Romanovskii[3] treated it as a bimolecular (BM) process. A sharp contradiction arises then. We do not know what makes this sharp contradiction and what the real situation is. To solve this problem estimation of real RRRC in photoluminescence decay is required. For this purpose samples of ZnS:Cu,Co have been prepared using the method in Ref.[4] and the photoluminescence decay analysed on the basis of quasi-equilibrium model proposed by Adirovich;[1] and the real value of RRRC of that sample has been determined to be intermediate between ∞ (corresponding to MM case) and 0 (corresponding to BM case). It turns out that the assessments of MM and BM reactions[2,3] represent only two extreme cases. Due to the popularity of TL, there are a lot of works in this field.[5−17] All effort is made to minimize the discrepancy between the analysed result and the real values. For example, Aramu *et al.*[8] proposed that the number of ionized centres is equal to that of traps; this is in fact equivalent to the assumption of MM process. May and Partridge[6] introduced the 'general order b' for kinetics, where b is a constant with $1 < b < 2$, while the physical meaning of b is not clear. The methods proposed by Garlick and Gibson,[7] Gobrecht and Hofmann,[9] Chen *et al*, [10,11] Mochen and Chen,[12] Shenker and Chen,[13] Maharil and Kathuria,[14] Mandowski and Swiatek,[15] and Haraneth *et al*[16] were all based on one of the three assumed kinetics: namely first order, some intermediate fixed order or second order kinetics. All these assumptions were connected to a fixed number. Some authors determined this kinetic order by other method, but they determined only the general range 1, b or 2, not the real numerical value of relative ratio of electron recombination to electron capture. Mandowski and Swiatek noticed the importance of the probability ratio of recombination to capture σ_0/σ in the regions of MM or BM kinetics, but not the ratio of recombination to capture $\sigma_0 n/\sigma(v-n)$ ($\sigma_0 n$ represents the recombination, and $\sigma(v-n)$ the capture), actually only the rate itself is responsible for the determination of the kinetic orders. Sakurai[17] used four parameters to fit the experimental glow curve, since the number of unknown parameters for this try and error method is too large. After the invention of new phosphors with persistent luminescence the study on long after-glow phenomenon has attracted much attention again.[18−25] However, the reasonable application of TL analysis is still scarce.

2. Theoretical analysis

In this paper we shall use a concrete sample to show the necessity of simultaneous determination of trap depth and RRRC which changes with time. This physical idea may be clearly expressed by rate equations. Based on the model of energy band and the quasi-equilibrium approximation proposed by Adirovich,[1] we investigate the TL of ZnS: Cu, Co in which the effective trap has only one depth.[26] In this case the process of TL may be described with the following rate equations.

At an arbitrary time the intensity of luminescence is expressed as

$$-\frac{\mathrm{d}n}{\mathrm{d}t} = \sigma_0 nuN, \tag{1}$$

$$\frac{\mathrm{d}n_1}{\mathrm{d}t} = \sigma(v-n_1)uN - p\mathrm{e}^{-\varepsilon/kT}n_1, \tag{2}$$

where n is the concentration of ionized luminescent centres, v is the concentration of total traps, n_1 is the concentration of filled traps, σ_0 and σ are the probabilities of recombination with ionized centres and that of capture by traps for conduction electrons respectively, t is time. N is the concentration and u is the velocity of conduction electrons, ε is the trap depth, T is the absolute temperature, and p is the escape factor.

Since the lifetime of electrons in conduction band is smaller than that in traps, we have $n = n_1$ and

$$\Big(1 + \frac{\sigma(v-n)}{\sigma_0 n}\Big)\frac{\mathrm{d}n}{\mathrm{d}t} = -p\,\mathrm{e}^{-\varepsilon/kT}n, \qquad (3)$$

or

$$\frac{1}{n}\Big(1 - \frac{\sigma}{\sigma_0} + \frac{\sigma v}{\sigma_0 n}\Big)\frac{\mathrm{d}n}{\mathrm{d}t} = -p\,\mathrm{e}^{-\varepsilon/kT}. \qquad (4)$$

Define γ as the ratio of light sum remaining in the phosphor at time t to the total light sum n_0 at $t = 0$, i.e., the percentage of remaining light sum in the phosphor at time t. $n(t) = \gamma n_0$, where the light sums $n(t)$ and n_0 can be measured accurately from the TL curve.

Denoting

$$\bar{n}_0 = \frac{\sigma_0 n_0}{\sigma v},$$

we have

$$\ln\left(\frac{1 + \big(1 - \frac{\sigma}{\sigma_0}\big)\gamma\bar{n}_0}{\gamma^2 n_0 \bar{n}_0}\Big(-\frac{\mathrm{d}n}{\mathrm{d}t}\Big)\right) = \ln p - \frac{\varepsilon}{k}\cdot\frac{1}{T}. \qquad (5)$$

Because n_0 and $\bar{n}_0$ in the denominator of the first term are constants in this experiment, they can be included in $\ln p$ and written as another constant C. Thus

$$\ln\left(\frac{1 + \Big(1 - \frac{\sigma}{\sigma_0}\Big)\gamma\bar{n}_0}{\gamma^2}\Big(-\frac{\mathrm{d}n}{\mathrm{d}t}\Big)\right) = C - \frac{\varepsilon}{k}\frac{1}{T}\,. \qquad (6)$$

This equation clearly shows that the brightness at any point on the glow curve depends on the simultaneous effect of RRRC and ε. Generally, TL curve is obtained by raising the temperature linearly, i.e. $\mathrm{d}T/\mathrm{d}t = \beta = \mathrm{constant}$. When the light intensity $(-\mathrm{d}n/\mathrm{d}t)$ of TL reaches its maximum, the first derivative of light intensity is zero, or the second derivative of n is zero. We have

$$\varepsilon = \left\{\frac{(2 + (1 - \sigma/\sigma_0)\gamma\bar{n}_0)}{\gamma\big(1 + (1 - \sigma/\sigma_0)\gamma\bar{n}_0\big)}\frac{1}{\beta n_0}\Big(-\frac{\mathrm{d}n}{\mathrm{d}t}\Big)kT^2\right\}_m. \qquad (7)$$

The subscript m denotes that every variable in the bracket must be the value at the maximum of TL.

From Eq.(7) we notice that the error of the estimated trap depth may be as large as nearly 100% if we assume an improper value of $\bar{n}_0$ ($\bar{n}_0$may vary from 0 to ∞, $\bar{n}_0 \approx 0$ corresponds to BM process, $\bar{n}_0 \to \infty$ corresponds to MM process). We must find the real value of $\bar{n}_0$. For example, let

$$E = \left\{\frac{1}{\gamma\beta n_0}\Big(-\frac{\mathrm{d}n}{\mathrm{d}t}\Big)kT^2\right\}_m,$$

if $\bar{n}_0 \to \infty$, we have $\varepsilon = E$, if $\bar{n}_0 \to 0$, we have $\varepsilon = 2E$. In other words, if we assume that TL curve obeys MM rule, we obtain a trap depth E, but for the same TL curve if we assume that the decay obeys BM rule, the trap depth will be $2E$. This means that when we analyse the same TL curve if we improperly treat a MM luminescence ($\bar{n}_0 \to \infty$) as BM process ($\bar{n}_0 \to 0$), the error is nearly 100%. Equation (7) is correct, but if the assumption is deviated from the actual value of $\bar{n}_0$, the result obtained is wrong. This situation shows again that the true value of trap depth can be obtained only if the value of $\bar{n}_0$ is exactly known. The value of ε and $\bar{n}_0$ should be determined simultaneously. In this paper we propose a reasonable method for determining the trap depth and the ratio of the rate of recombination to that of capture simultaneously.

3. Experiment

We prepared the samples ZnS: Cu, Co entirely according to the prescription and conditions stated in Refs. [4] and [5] in order to use the data of σ/σ_0 in Ref. [5].

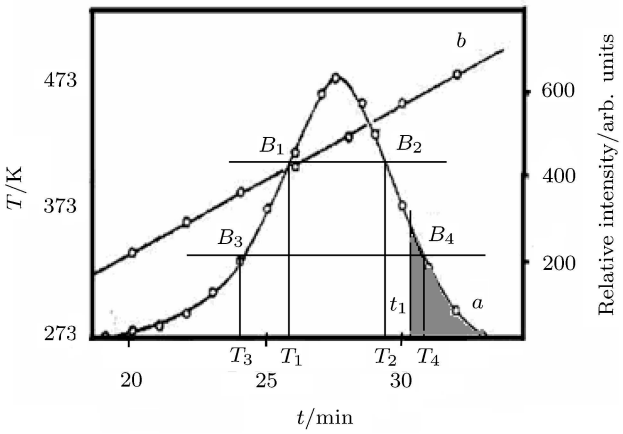


Fig.1. Curve *a*: TL of ZnS: Cu, Co; Curve *b*: Dependence of temperature on time.

Thus we prepared powder ZnS doped with 10^{-6}Cu g/g and 10^{-5} Co g/g and then mixed with 5 wt% $CaCl_2$. This mixture was sintered at 1100 ℃

for 30 min. The phosphor was excited by 366 nm radiation at room temperature. Then let the luminescence decay for 15 min and lowered the temperature of phosphor down to liquid nitrogen temperature. After this we raised the temperature of phosphor from 0 ℃ to 196 ℃ at constant rate 9.2 ℃/min, and obtained the TL curve with only one emission peak to study the single trap model, as shown in Fig.1.

4. Discussions

We use the following methods to find the interrelated important unknown parameters $\bar{n}_0$ and ε in TL of ZnS: Cu, Co.

A) Divide the TL curve of ZnS: Cu, Co into two segments by one vertical line corresponding to different temperature. The area between a vertical line t_1 and the end of TL curve is the remaining light sums in the phosphor at t_1 (see Fig.1). All the different areas are expressed by a series of γ values. Using try and error method and choosing an arbitrary value of $\bar{n}_0$, we put it together with one of the series values of γ into Eq.(6) with $\sigma/\sigma_0 \approx 0.005$ given in Ref.[5] which can be neglected. For different γ value, we obtain a series of calculated values of $\ln[(1+\gamma\bar{n}_0)B_\gamma/\gamma^2]$ at different $1/T$ values. These data are represented by points with ordinate $\ln[(1+\gamma\bar{n}_0)B_\gamma/\gamma^2]$ and abscissa $1/T$. Connect these points under the same $\bar{n}_0$ and different temperatures. If the value of $\bar{n}_0$ is incorrectly chosen, we shall obtain a curve. When $\bar{n}_0$ is larger than the correct one, the line is an upswept curve and when $\bar{n}_0$ is less than the correct one, then the line is a downbent curve. Only when the value of $\bar{n}_0$ is correctly chosen, we shall obtain a straight line (see in Fig.2). The proper value of $\bar{n}_0$ is thus determined by fitting the experimental data.[27] After the determination of $\bar{n}_0$, ε is determined from the slope of this straight line. Thus we determine both $\bar{n}_0$ and trap depth ε simultaneously. The straight line appears for $\bar{n}_0 \approx 3$, which means that the initial ratio of the rate of recombination to that of capture is $\bar{n}_0 \approx 3$. Then it decreases towards zero. But due to the continuous increase of temperature the traps are finally evacuated. The trap depth ε is calculated from the slope of this straight line and is found to be 0.83 eV.

B) The trap depth can also be calculated from Eq.(7) by using the parameters $\bar{n}_0 \approx 3$, $\beta = 9.2$ ℃/min and $-(\mathrm{d}n/\mathrm{d}t)_m = B_m$. $B_m = 460$ (arb. units) (Both B_m and n_0 are kept in the same arbitrary units). The calculated $\varepsilon = 0.86$ eV.

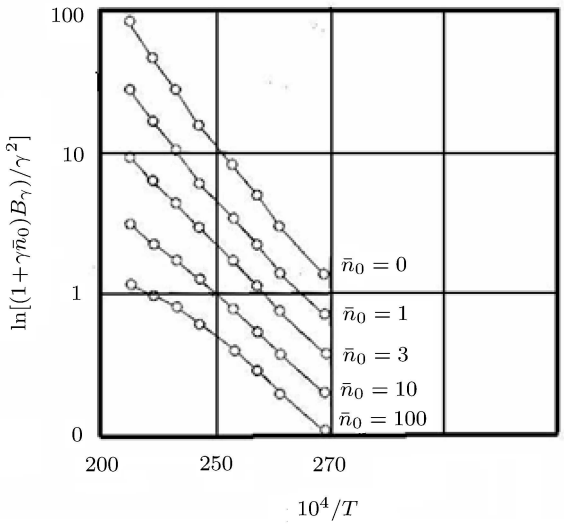


Fig.2. Dependence of $\ln[(1+\gamma\bar{n}_0)B_\gamma/\gamma^2]$ on $1/T$ (The ratio of the probability of recombination to that of capture is 0.005 and is neglected).[27]

C) We notice from Fig.1 that the TL curve has a maximum, and on its left and right sides we may find points of equal intensity. Thus we draw a horizontal line to cut the TL curve at two points T_1 and T_2 where the light intensity is identical, $B_1 = B_2 = B$. From Eq.(5) we have two points located at

$$\left\{\ln\Big(\frac{1+(1-\sigma/\sigma_0)\gamma_1\bar{n}_0}{\gamma_1^2}B_1\Big), \frac{1}{T}\right\}$$

and

$$\ln\Big(\frac{1+(1-\sigma/\sigma_0)\gamma_2\bar{n}_0}{\gamma_2^2}B_2\Big), \frac{1}{T_2}\Big\}.$$

Put the coordinates of these two points into Eq.(5) separately and let one of the equations minus the other. We obtain

$$\ln\left\{\frac{\gamma_2^2(1+(1-\sigma/\sigma_0)\gamma_1\bar{n}_0)}{\gamma_1^2(1+(1-\sigma/\sigma_0)\gamma_2\bar{n}_0}\right\} = \Big(\frac{1}{T_2}-\frac{1}{T_1}\Big)\frac{\varepsilon}{k}. \quad (8)$$

Then draw another similar horizontal line at a lower level to intersect the TL curve. We have another two points located at

$$\left\{\ln\Big(\frac{1+(1-\sigma/\sigma_0)\gamma_3\bar{n}_0}{\gamma_3^2}B_3\Big), \frac{1}{T}\right\}$$

and

$$\left\{\ln\Big(\frac{1+(1-\sigma/\sigma_0)\gamma_4\bar{n}_0}{\gamma_4^2}B_4\Big), \frac{1}{T}\right\}.$$

Put the coordinates of these two points into Eq.(6) separately and let one minus the other, we obtain

$$\ln\left\{\frac{\gamma_4^2(1+\big(1-\sigma/\sigma_0)\gamma_3\bar{n}_0)}{\gamma_3^2(1+(1-\sigma/\sigma_0)\gamma_4\bar{n}_0}\right\} = \Big(\frac{1}{T_4}-\frac{1}{T_3}\Big)\frac{\varepsilon}{k}. \quad (9)$$

From Ref. [3] the value of σ/σ_0 is found to be 0.005 for ZnS:Cu, Co. Since $\gamma\bar{n}_0$ is always bigger than zero, if we neglect σ/σ_0, the error is less than 0.005 and then the equation is simplified as two independent equations with two unknown parameters. These parameters might be found by solving this group of equations.

We use the software 'getdata' to obtain the coordinates of each point on the glow curve. Then we use software 'AUTOCAD' to find the area under the curve between any vertical line at t and the end point. Putting the data into Eqs.(8) and (9) and using the software 'Matlab', then we can gain the value of $\bar{n}_0$ and ε. The average of them is $\bar{n}_0 = 2.6$, $\varepsilon = 0.86$ eV. The error analysis by means of 'Mathematica' shows that the square root error of $\bar{n}_0$ is 8.7×10^{-3}, that of ε is 1.5×10^{-5}; and the standard error of $\bar{n}_0$ is 9.3×10^{-3}, that of ε is 3.9×10^{-3}.

5. Conclusion

A) TL is in fact a luminescence decay process with increasing temperature. The effect of trap ε is tangled with RRRC. Without knowing the exact value of RRRC it is impossible to reasonably determine the value of trap depth ε. Since RRRC is always changing with time, incorrect assumption of a constant order of luminescence may lead to an error as large as 100%.

B) We have proposed three methods for reasonably determining the trap depth and the ratio of the rate of recombination to that of capture from a single TL curve simultaneously in the case of ZnS: Cu, Co with known σ/σ_0. The trap depth is found to be 0.83 eV, and the relative ratio of the rate of recombination to that of capture is found to be nearly 3.

C) The concentration of traps is approximately 67 times larger than that of excited luminescent centres from

$$\bar{n}_0 = \frac{\sigma_0 n_0}{\sigma v}\,, \quad \frac{n_0}{v} = \bar{n}_0 \Big/ \left(\frac{\sigma_0}{\sigma}\right) = \frac{3}{200} \approx \frac{1}{67}\,.$$

D) The above-mentioned methods are applicable to traps of only one depth. But in the case of several peaks we can still use it for the deepest trap, if we excite the sample at temperatures higher than that corresponding to the next deep level. Then the analysis is the same as that for one depth. Note that this method is applicable only when no external quenching occurs during TL, i.e., no annihilation of ionized centres by electrons in valence band.

E) In the analysis we use the known value of σ/σ_0. If σ/σ_0 is unknown, the third method may be used to find a third equation and another level of brightness. Thus we have three independent equations for finding three unknowns.

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