

Accuracy (definition)

Errors of measurement are of two types, random and systematic. For a given set of measurement conditions a source of random error is variable in both magnitude and sign, whereas a source of systematic error has a constant relative magnitude and is always of the same sign.

The accuracy is affected by both systematic and random uncertainties.

Accuracy is related to the closeness of a measurement, within certain limits, with the true value of the quantity under measurement. For instance, the accuracy of dose determination by TLD is given by the difference between the measured value of the dose (TL reading) and the true dose given to the dosimeter.

A method of combining systematic and random uncertainties has been suggested in a BCS document: both systematic and random errors are combined by quadratic addition but the result for systematic errors is multiplied by 1.13. This factor is necessary to ensure a minimum confidence level of 95%.

Activation energy (definition and properties)

It is the energy, E , expressed in eV, assigned to a **metastable state** or level within the forbidden band gap between the **conduction band** (CB) and the **valence band** (VB) of a crystal. This energy is also called trap depth. The metastable level can be an electron trap, near to the CB, or a hole trap, near the VB, or a **luminescence centre**, more or less in the middle of the band gap. The metastable levels are originated by **defects** of the crystal structure. A crystal can contain several kinds of traps and luminescence centres. If E is such that $E > \text{several } kT$, where k is the Boltzmann's constant, then the trapped charge can remain in the trap for a long period. For an electron trap, E is measured, in eV, from the trap level to the bottom of the CB. For a hole trap, it is measured from the trap to the top of the VB.

Fig. 1 shows the simplest band structure of an insulator containing defects acting as traps or luminescence centres.

Bombarding the solid with an ionizing radiation, this produces free charges which can be trapped at the metastable states. Supposing the solid previously excited is heated, a quantity of energy is supplied in the form of thermal energy and the trapped charges can be released from the traps. The rate of such thermally stimulated process is usually expressed by the **Arrhenius** equation which leads to the concept of the activation energy, E , which can be seen as an energy barrier which must be overcome to reach equilibrium.

Considering the maximum condition using the first order kinetics:

$$\frac{\beta \cdot E}{k \cdot T_M^2} = s \exp\left(-\frac{E}{kT_M}\right)$$

it is easily observed that T_M increases as E increases. In fact, for $E \gg kT_M$, T_M increase almost linearly with E . This behaviour agree to the Randall-Wilkins model where, for deeper traps, more energy and, in turn, a higher temperature, is required to detrapp the electrons [1-4].

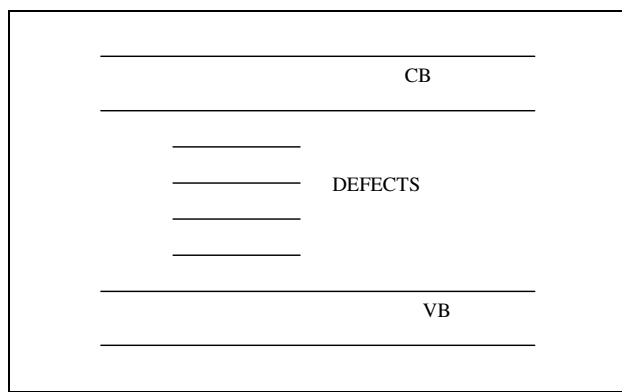


Fig. 1. A simple band structure of an isolant with defect levels in the band gap.

References

1. Bräunlich P. in *Thermally Stimulated Relaxion in Solids*, P. Bräunlich editor, Springer-Verlag, Berlin (1979)
2. Chen R. and McKeever S.W.S., *Theory of Thermoluminescence and Related Phenomena*, World Scientific (1997)
3. Chen R. and Kirsh Y., *Analysis of Thermally Stimulated Processes*, Pergamon Press (1981)
4. McKeever S.W.S., *Thermoluminescence of Solids*, Cambridge University Press (1985)

Activator

There are several luminescent materials but not all are efficient enough for practical purposes. To enhance the luminescence efficiency of the material is necessary to add an element, called activator (i.e., Dy in CaSO_4), to the host crystal. The activator acts then as **luminescent centre**.

Adirovitch model

Adirovitch, in 1956, used a set of three differential equations to explain the decay of phosphorescence in the general case. The same model has been used by Haering-Adams (1960) and Halperin-Braner (1960) to describe the flow charge between localized energy levels and delocalized bands during trap emptying. The energy level diagram is shown in Fig. 1.

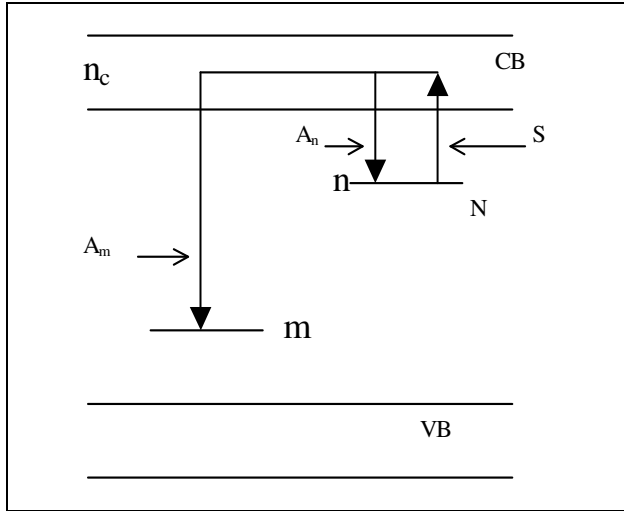


Fig. 1. Energy level diagram concerning the phosphorescence decay according to Adirovitch. The meaning of the symbols is given in the text.

With the assumption that retrapping of electrons occurs into trapping states of the same kind as those from which they had been released, the intensity of emission, I , is given by

$$I = -\frac{dm}{dt} = A_m m n_c \quad (1)$$

where

m is the concentration of recombination centers (holes in centers), (cm^{-3});

n_c is the concentration of free electrons in the conduction band, (cm^{-3});

A_m is the recombination probability ($\text{cm}^3 \text{sec}^{-1}$).

This equation states that the recombination rate is proportional to the number of free electrons, n_c , and the number of active recombination centers, m .

A second equation deals with the population variation of electrons in traps, n (cm^{-3}), and it takes into account of the excitation of electrons into the conduction band as well as the possible retrapping. Then we have:

$$\frac{dn}{dt} = -sn \exp\left(-\frac{E}{kT}\right) + n_c (N - n) A_n \quad (2)$$

where A_n ($\text{cm}^3 \text{ s}^{-1}$) is the retrapping probability and N (cm^{-3}) is the total concentration of traps. A_m and A_n are assumed to be independent of temperature.

The third equation relates to the charge neutrality. It can be expressed as

$$\frac{dn_c}{dt} = \frac{dm}{dt} - \frac{dn}{dt} \quad (3)$$

or better, using Eq. (1) and (2), as

$$\frac{dn_c}{dt} = sn \exp\left(-\frac{E}{kT}\right) - n_c mA_m - n_c (N - n) A_n \quad (4)$$

Eq. (4) states that the rate of change of n_c is given by the rate of release of electrons from N , minus the rate of recombination in m and retrapping in N .

While Adirovitch used the previous equations to explain the decay of phosphorescence, Halperin and Braner were the formers to apply the same equations to the case of thermoluminescence, that is to say when the light emission is measured during the heating of the sample, when one trapping state and one kind of recombination center are involved.

Two basic assumptions have been made for solving the previous set of equations:

$$n_c \ll n \quad (5)$$

and

$$\left| \frac{dn_c}{dt} \right| \ll \left| \frac{dn}{dt} \right| \quad (6)$$

The condition (6) means that the concentration of carriers in the conduction band does not change; that is to say

$$dn_c = 0 \quad (7)$$

In this case Eq. (4) gets

$$n_c = \frac{sn \exp\left(-\frac{E}{kT}\right)}{mA_m + (N-n)A_n} \quad (8)$$

and then the intensity is given by

$$I = -\frac{dm}{dt} = \frac{sn \exp\left(-\frac{E}{kT}\right)}{mA_m + (N-n)A_n} \cdot mA_m \quad (9)$$

Introducing the retrapping-recombination cross-section ratio

$$\sigma = \frac{A_n}{A_m} \quad (10)$$

equation (9) becomes

$$I = -\frac{dm}{dt} = ns \exp\left(-\frac{E}{kT}\right) \left[1 - \frac{\sigma(N-n)}{\sigma(N-n) + m} \right] \quad (11)$$

Equation (11) gets the general one-trap equation (GOT) for the TL intensity. The term preceding the square brackets is the number of electrons thermally released to the conduction band per unit time. The term in square brackets is the fraction of conduction band electrons undergoing recombination. From this equation it is possible to obtain the first and second order kinetics equations.

Indeed, the first order kinetics is the case when recombination dominates and this means that

$$mA_m \gg (N-n)A_n \quad (12)$$

or

$$\sigma = 0 \quad (13)$$

The equation of intensity becomes then

$$I = -\frac{dm}{dt} = ns \exp\left(-\frac{E}{kT}\right) \quad (14)$$

The assumption (7) gives

$$\frac{dm}{dt} = \frac{dn}{dt} \quad \text{or} \quad m = n + \text{const}$$

and so Eq. (14) becomes

$$I = -\frac{dn}{dt} = ns \exp\left(-\frac{E}{kT}\right) \quad (15)$$

that is the same of equation of the **first order kinetics**.

The second order expression can be derived from Eq. (11) using two assumptions which both include the restrictive assertion $m = n$.

Remembering the **Garlick and Gibson's retrapping assumption**, the first condition can be written as

$$mA_m \ll (N-n)A_n$$

and then the intensity is given by

$$I = -\frac{dm}{dt} = \frac{mA_m ns \exp\left(-\frac{E}{kT}\right)}{(N-n)A_n} \quad (16)$$

Secondly, assuming that the trap is far from saturation, which means $N \gg n$, we obtain

$$I = -\frac{dm}{dt} = \frac{mA_m ns \exp\left(-\frac{E}{kT}\right)}{NA_n} \quad (17)$$

Using the condition $m = n$ the last equation becomes

$$I = -\frac{dn}{dt} = \frac{n^2 s A_m \exp\left(-\frac{E}{kT}\right)}{NA_n} \quad (18)$$

which, with $s' = sA_m/NA_n$, is the **Garlick and Gibson equation**.

Assuming now equal recombination and retrapping probabilities $A_m = A_n$, as suggested by Wrzesinska, one obtains the same equation of Garlick and Gibson with $s' = s/N$:

$$I = -\frac{dn}{dt} = n^2 s' \exp\left(-\frac{E}{kT}\right) \quad (19)$$

Reference

Adirovitch E.I.A., J. Phys. Rad. **17** (1956) 705

Afterglow

Afterglow is the term used to indicate the luminescence emitted from a TL phosphor immediately after irradiation. If this effect is thermally dependent, according to the equation

$$\tau = s^{-1} \exp\left(\frac{E}{kT}\right)$$

it is more properly termed phosphorescence.

The emission spectrum of the afterglow is the same as that of thermoluminescence: this fact indicates that the same luminescence centers are involved. Zimmerman found a correlation between the anomalous (athermal) fading and the afterglow [1-3].

References

1. Zimmermann D.N., Abstract Symp. Archaeometry and Archaeological Prospection, Philadelphia (1977)
2. Zimmermann D.N., PACT **3** (1979) 257
3. Visocekas R., Leva T., Marti C., Lefauchaux F. and Robert M.C., Phys. Stat. Sol. (a) **35** (1976) 315

Aluminium oxide (Al₂O₃)

Chromium substituting for some of the aluminum atoms in Al₂O₃ changes sapphire into ruby, which exhibits TL properties studied since the sixties [1-5].

Investigations on the TL of ruby, whose effective atomic number is 10.2, are performed by using synthetic crystals of Al₂O₃ containing various known concentrations of Cr₂O₃ (typically 0.01 to 0.2 wt%).

TL glow curve of ruby consists of a main glow peak at 347°C (shifting toward lower temperatures for high exposures) and a less intense peak at 132°C (in the same region as the peak reported for sapphire). High chromium concentrations cause a relative increase in the lower temperature portion of the glow curve.

References

1. Gabrysh A.F., Eyring H., Le Febre V. and Evans M.D., J. Appl. Phys. **33** (1962) 3389
2. Maruyama T., Matsuda Y. and Kon H., J. Phys. Soc. Japan **18-II** (1963) 315
3. Buckman W.G., Philbrick C.R. and Underwood N., U.S. Atomic Energy Commission Rep. CONF-680920 (1968)
4. Hashizume T., Kato Y., Nakajima T., Yamaguchi H. and Fujimoto K., Health Phys. **23** (1972) 855
5. Watson J.E., Health Phys. **31** (1976) 47

Annealing (definition)

Annealing is the thermal treatment needed to erase any irradiation memory from the dosimetric material.

Some thermoluminescent material requires a complex annealing procedure. LiF:Mg,Ti is one of them. It requires a high temperature anneal, followed by a low temperature anneal. Generally speaking the high temperature anneal is required to clear the **dosimetric traps** of residual signal which may cause unwanted backgrounds during subsequent use of the dosimeters. The low temperature anneal is required to stabilize and aggregate low temperature traps in order to enhance the sensitivity of the main dosimetry traps and to reduce losses of radiation-induced signal due to thermal or optical fading during use. The combination of these two anneals is termed standard anneal.

For lithium fluoride the standard annealing consists in a high temperature anneal at 400°C during 1 hour followed by a low temperature thermal treatment for 20 hours at 80°C. In some laboratories, annealing at 100°C for 2 hours has been used instead of the longer anneal at 80°C.

The TL properties exhibited by a phosphor strongly depend upon the kind of thermal annealing experienced by it prior to the irradiation. It is also true, in general, that more defects are produced at higher temperatures of annealing.

The number of defects depends also on the cooling rate employed to cool the phosphor to the ambient temperature.

Once the best annealing procedure has been determined, i.e. the highest TL response with the lowest standard deviation, the same procedure must be always followed for reproducible results in TL applications [1,2]

References

1. Driscoll C.M.H., National Radiological Protection Board, Tech. Mem. 5(82)
2. Busuoli G. in Applied Thermoluminescence Dosimetry, ISPRA Courses, Edited by M. Oberhofer and A. Scharmann, Adam Hilger publisher (1981)

Annealing (general considerations)

Before using a thermoluminescent material for dosimetric purposes, it has to be prepared. To prepare a TL material means to erase from it all the information due to any previous irradiation, i.e., to restore in it the initial conditions of the crystal as they were before irradiation. The preparation has also the purpose of to stabilising the trap structure.

In order to prepare a thermoluminescent material for use, it is needed to perform a thermal treatment, usually called **annealing** [1,2], carried out in oven or/and furnace, which consists of heating up the TL samples to a predetermined temperature, keeping them at that temperature for a predetermined period of time and then cooling down the samples to room temperature. It has to be stressed that the thermal history of the thermoluminescent dosimeters is crucial for the performance of any TLD system.

There is a large number of thermoluminescent materials, however the annealing procedures are quite similar. Just few materials, like LiF:Mg,Ti, need a complex annealing procedure.

The thermal treatments normally adopted for the TLDs can be divided into three classes:

- **initialisation treatment:** this treatment is used for new (fresh or virgin) TL samples or for dosimeters which have not been used for long time. The aim of this thermal treatment is to stabilise the trap levels, so that during subsequent uses the intrinsic background and the sensitivity are both reproducible. The time and temperature of the initialisation annealing are, in general, the same as those of the standard annealing.
- **erasing treatment or standard annealing** (also called **pre-irradiation annealing** or **post-readout annealing**): this treatment is used to erase any previous residual irradiation effect which is supposed to remain stored in the crystal after the readout. It is carried out before using the TLDs in new measurements. The general aim of this thermal treatment is to bring back the traps - recombination centers structure to the former one obtained after the initialisation procedure. It may consist of one or two thermal treatments (in latter case, at two different temperatures).
- **post-irradiation or pre-readout annealing:** this kind of thermal treatment is used to erase the low-temperature peaks, if they are found in the glow-curve structure. Such low-temperature peaks are normally subjected to a quick thermal decay (fading) and possibly must not be included in the readout to avoid any errors in the dose determination.

In all cases, value and reproducibility of the cooling rate after the annealing are of great importance for the performance of a TLD system. In general, the TL sensitivity is increased using a rapid cool down. It seems that the sensitivity reaches the maximum value when a cooling rate of 50-100°C/s is used. To obtain this, the TLDs must be taken out of the oven after the pre-set time of annealing is over and placed directly on a cold

metal block. The procedure must be reproducible and unchanged during the whole use of the dosimeters.

It must be noted that the thermal procedures listed above can be carried out in the reader itself. This is important for TL elements embedded in plastic cards as the dosimeters used for large personnel dosimetry services. In fact, the plastic cards are not able to tolerate high temperatures and the in-reader annealing is shortened to a few seconds. However, its efficiency is very low when high dose values are involved. The in-reader annealing procedure should be used only if the dose received by the dosimeter is lower than 10 to 20 mGy. Driscoll suggests in this case a further annealing in oven during 20 hours at 80°C for cards holding LiF:Mg,Ti; at this temperature the plastic holder does not suffer any deformation. Any way, excluding cards, for bare TL solid chips or TL materials in powder form, the annealing must be performed in an oven.

References

1. Busuoli G. in *Applied Thermoluminescence Dosimetry*, ISPRA Courses, Edited by M. Oberhofer and A. Scharmann, Adam Hilger publisher (1981)
2. Driscoll C.M.H., Barthe J.R., Oberhofer M., Busuoli G. and Hickman C., *Rad. Prot. Dos.* **14**(1) (1986) 17

Annealing procedures

When a new TL material is going to be used for the first time, it is necessary to perform at first an annealing study which has three main goals:

- to find the good combination of annealing temperature and time to erase any effect of previous irradiation,
- to produce the lowest intrinsic background and the highest sensitivity,
- to obtain the highest reproducibility for both TL and background signals.

The suggested procedures are the following:

1st procedure

- irradiate 10 TLDs samples to a test dose in the range of the field applications,
- anneal the irradiated samples at a given temperature (e.g., 300°C) for a given period of time (e.g., 30 minutes),
- read the samples,
- repeat steps 1), 2) and 3) increasing the annealing temperature of 50°C each time up to the maximum value at which the residual TL (background) will remain constant as the temperature increases,

- plot the data as shown in Fig. 1. As it can be observed, after a threshold temperature value, i.e., T_c , the residual TL signal remains constant,
- repeat now the procedure, keeping constant the temperature at the value T_c and varying the annealing time by steps of 30 minutes and plot the results. The plot should be similar to the previous one,
- choose now the best combination of temperature and time.
- carry out a reproducibility test to verify the goodness of the annealing, in the sense that background must be unchanged during the test.

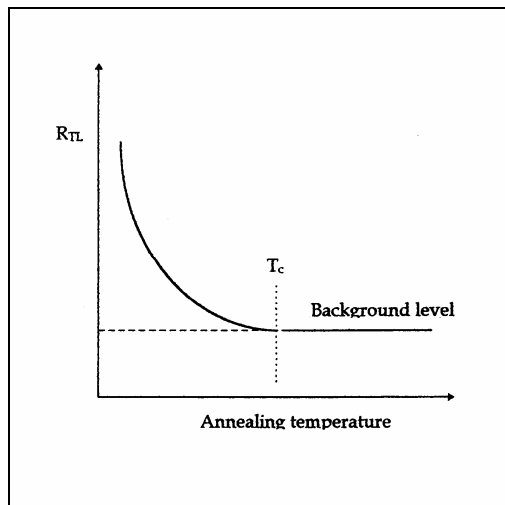


Fig. 1. Decrease of TL response, after irradiation, as a function of the annealing procedure.

2nd procedure

This procedure has been suggested by G. Scarpa [1] who used it for sintered Beryllium Oxide. With this procedure both informations concerning annealing and reproducibility are obtained at once. The procedure consists in changing the temperature, step by step, at a constant annealing time. After annealing at a given temperature, the samples are irradiated and then readout. For each temperature 10 samples are used, cycled 10 times. So that each experimental point in Fig. 2 is based on 100 measurements. From the figure it can be seen that the best reproducibility, i.e., the lowest standard deviation in %, is achieved at around 600°C , whereas the absolute value of the TL output is practically constant between 500 and 700°C . The same procedure can be now carried out for a constant temperature and changing the annealing time. Finally, as before, the best combination of time and temperature should give the optimum annealing procedure.

To be sure that the annealing procedure is useful at any level of dose, it is suggested to repeat the procedure at different doses, according to the specific use of the material.

Figs. 3 and 4 gave other examples of this procedure [2]. Each experimental point correspond to the average over ten samples. The annealing time at each temperature was 1 hr.

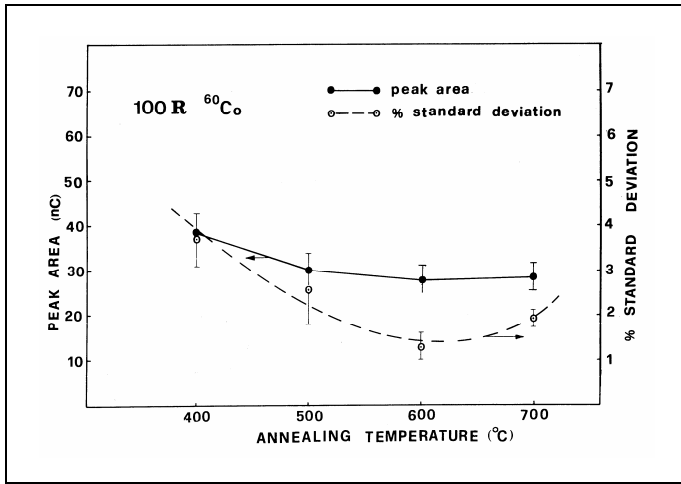


Fig. 2. TL emission (peak area) and corresponding S.D.% Vs annealing temperatures.

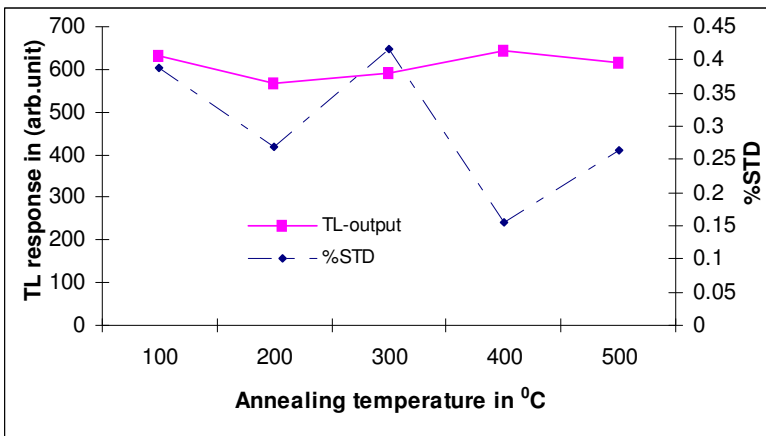


Fig. 3. Behaviour of the TL response and the corresponding standard deviation as a function of the annealing temperature (Ge-doped optical fibre).

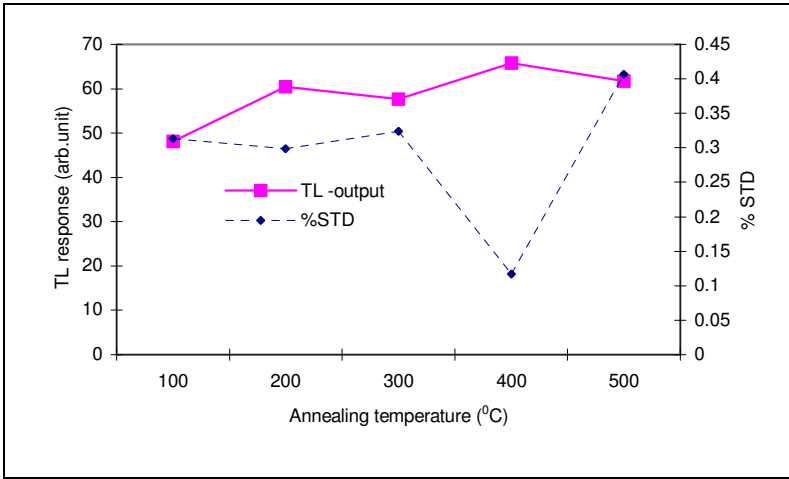


Fig. 4. Behaviour of the TL response and the corresponding standard deviation as a function of the annealing temperature (Eu-doped optical fibre).

The following Tables 1a, 1b and 1c list the annealing and the post-annealing procedures used for most of the thermoluminescent materials.

material	annealing procedure	
	in oven	in reader
LiF:Mg,Ti (TLD100,600,700)	1 h at 400°C + 2 h at 100°C [4] or 1 h at 400°C + 20 h at 80°C [4] fast anneal: 15 min at 400°C +10 min at 100°C [5]	30 sec at 300- 400°C (+ 20 h at 80°C in oven) [3]
LiF:Mg,Ti in PTFE (polytetrafluoroethylene)	1 h at 300°C + 20 h at 80°C [6]	30 sec at 300°C (+ 20 h at 80°C in oven)
LiF:Mg,Ti,Na (LiF-PTL)	30 min at 500°C + fast cooling [7]	
LiF:Mg,Cu,P (GR-200A)	10 min at 240°C [8-11] or 15 min at 240°C [12]	30 sec at 240°C
CaF ₂ :Dy (TLD-200)	1 h at 600°C or 30 min at 450°C or h at 400°C or 1 h at 400°C or 1 h at 400°C + 3 h at 100°C [13,14]	30 sec at 400°C
CaF ₂ :Tm (TLD-300)	1½ - 2 h at 400°C or 30 min at 300°C [15]	
CaF ₂ :Mn (TLD-400)	30-60 min at 450-500°C [16]	
CaSO ₄ :Dy (TLD-900)	½ - 1 h at 400°C	
CaSO ₄ :Tm	30 min-1 h at 400°C (PTFE: 2 h at 300°C)	
BeO (Thermal ox 995)	15 min at 400 or 600°C [17,18]	30 sec at 400°C
Li ₂ B ₄ O ₇ :Mn (TLD-800)	15 min - 1 h at 300°C	
Li ₂ B ₄ O ₇ :Mn,Si	30 min at 400°C [31]	
Li ₂ B ₄ O ₇ :Cu	30 min at 300°C [31]	
Li ₂ B ₄ O ₇ :Cu,Ag	15 min - 1 h at 300°C	
Li ₂ B ₄ O ₇ :Cu,In	30 min at 300°C [31]	

Table 1a. Annealing treatments [3].

material	annealing procedure	
	in oven	in reader
α -Al ₂ O ₃ :C	1 h at 400°C + 16 h at 80°C	
Al ₂ O ₃ :Cr	15 min at 350°C	
Mg ₂ SiO ₄ :Tb	2 - 3 h at 500°C 1 h at 300°C	
MgB ₄ O ₇ :Dy/Tm	1 h at 500-600°C [19,20]	
MgB ₄ O ₇ :Dy,Na	30 min at 700°C + 30 min at 800°C or 2 h at 550°C [21,22] 1 hr at 400°C [32]	
CVD Diamond	½ h at 300°C [23]	
KMgF ₃ (various dopants)	1 hr at 400°C [24-28]	
semiconductor-doped Vycor glass	several seconds at 400°C	
RbCl:OH ⁻ RbCl:OH ⁻	30 min at 600°C [33]	

Table 1b. Annealing treatments [3].

material	pre-readout treatment (post-irradiation anneal)	
	in oven	in reader
LiF:Mg,Ti (TLD-100,600,700)	10 min at 100°C	20 sec at 160°C
LiF:Mg,Ti in PTFE	10 min at 100°C	10-20 sec at 160°C
LiF:Mg,Na (LiF-PTL)		10 sec at 130°C
LiF:Mg,Cu,P (GR-200A)	10 min at 130°C [29]	20-30 sec at 160°C [29]
CaF ₂ :Dy (TLD-200)	10 min at 110°C or 10 min at 115°C	16 sec at 160°C
CaF ₂ :Tm (TLD-300)	30 min at 90°C or 10 min at 115°C	16 sec at 160°C
CaSO ₄ :Dy (TLD-900)	20 - 30 min at 100°C or 5 min at 140°C	16 - 32 sec at 120°C
CaSO ₄ :Tm	20 - 30 min at 100°C	16 - 32 sec at 120°C
BeO (Thermalox 995)		1 min at 140°C
Li ₂ B ₄ O ₇ :Mn (TLD-800)	10 min at 100°C	
Li ₂ B ₄ O ₇ :Mn,Si		20 sec at 160°C
Li ₂ B ₄ O ₇ :Cu,Ag		20 sec at 160°C
Al ₂ O ₃ :Cr	15 min at 150°C	
MgB ₄ O ₇ :Dy/Tm		few sec at 160°C [30]
KMgF ₃ (various dopants)	30 - 60 min at 50°C [24-28]	

Table 1c. Post-irradiation treatments.

References

1. Benincasa G., Ceravolo L. and Scarpa G., CNEN RT/PROT(74)1
2. Youssef Abdulla, private communication
3. Driscoll C.M.H., Barthe J.R., Oberhofer M., Busuoli G. and Hickman C. Rad. Prot. Dos. **14**(1) (1986) 17

4. Scarpa G. in "Corso sulla termoluminescenza applicata alla dosimetria" University of Rome "La Sapienza", Italy, 15-17 February 1994
5. Scarpa G. in "IV incontro di aggiornamento e di studio sulla dosimetria a termoluminescenza" ENEA, Centro Ricerche Energia Ambiente, S.Teresa (La Spezia), Italy, 18-19 June 1984
6. Horowitz Y.S., "Thermoluminescence and thermoluminescent dosimetry" Vol. I, CRC Press, 1984
7. Portal G., Francois H., Carpenter S., Dajlevic R. Proc. 2nd Int. Conf. Lum. Dos., Gatlinburg USAEC Rep. Conf. 680920, 1968
8. Wang S., Cheng G., Wu F., Li Y., Zha Z., Zhu J., Rad. Prot. Dos. **14**, 223, 1986
9. Driscoll C.M.H., McWhan A.F., O'Hogan J.B., Dodson J., Mundy S.J., Todd C.D.T., Rad. Prot. Dos. **17**, 367, 1986
10. Horowitz Y.S., Horowitz A., Rad. Prot. Dos. **33**, 279, 1990
11. Zha Z., Wang S., Wu F., Chen G., Li Y., Zhu J., Rad. Prot. Dos. **17**, 415, 1986
12. Scarpa G. private communication 1991
13. Binder W., Cameron R.J., Health Phys. **17**, 613, 1969
14. Portal G., in Applied Thermoluminescence Dosimetry, ed. M. Oberhofer and A. Sharmann, Adam & Hilger, Bristol, 1981
15. Furetta C., Lee Y.K., Rad. Prot. Dos., **5**, 57, 1983
16. Ginther R.J., Kirk R.D., J. Electrochem. Soc., **104**, 365, 1957
17. Tochilin E., Goldstein, N., Miller W.G., Health Phys. **16**, 1, 1969
18. Busuoli G., Lembo L., Nanni R., Sermenghi I. Rad. Prot. Dos. **6**, 317, 1984
19. Barbina V., Contento G., Furetta C., Molisan C., Padovani R., Rad. Eff. Lett. **67**, 55, 1981
20. Barbina V., Contento G., Furetta C., Padovani R., Prokic M., Proc Third Int. Symp. Soc. Radiol. Prot. (Inverness) 1982
21. Driscoll C.M.H., Mundy S.J., Elliot J.M., Rad. Prot. Dos. **1**, 135, 1981
22. Furetta C., Weng P.S., Hsu P.C., Tsai L.J and Vismara L., Int. Conf. Rad. Dos. & Safety, Taipei, Taiwan, 1997
23. Borch E., Furetta C., Kitis G., Leroy C. and Sussmann R.S., Rad. Prot. Dos. **65**(1-4), 291, 1996
24. Furetta C., Bacci C., Rispoli B., Sanipoli C. and Scacco A., Rad. Prot. Dos. **33** 107, 1990
25. Bacci C., Fioravanti S., Furetta C., Missori M., Ramogida G, Rossetti R, Sanipoli C. and Scacco A., Rad. Prot. Dos. **47**, 1993, 277
26. Furetta C., Ramogida G., Scacco A, Martini M. and Paravisi S., J. Phys. Chem. Solids **55**, 1994, 1337
27. Furetta C., Santopietro F., Sanipoli C. and Kitis G., Appl. Rad. Isot. **55**, 2001 533
28. Furetta C., Sanipoli C. and Kitis G., J. Phys D: Appl. Phys. **34**, 2001, 857
29. Scarpa G., Moscati M., Soriani A. in "Proc. XXVII Cong. Naz. AIRP, Ferrara, Italy, 16-18 Sept., 1991
30. Driscoll C.M.H., Mundy S.J. and Elliot J.M., Rad. Prot. Dos. **1** (1981) 135
31. Kitis.G, Furetta C. Prokic M. and Prokic V., J. Phys. D: Appl. Phys. (2000) 1252
32. Furetta C., Prokic M., Salamon R. and Kitis G., Appl. Rad. Isot. **52** (2000) 243
33. Furetta C., Laudadio M.T., Sanipoli C., Scacco A., Gomez Ros J.M. and Correcher V., J. Phys. Chem. Solids **60** (1999) 957

Anomalous fading

The expected mean lifetime, τ , of a charge in a trap having a depth E is given by the following equation, according to a first order kinetics:

$$\tau = s^{-1} \exp\left(\frac{E}{kT}\right)$$

where s is the frequency factor and T is the storage temperature.

For many materials it is often found that the drainage of traps is not accounted for by the previous equation: i.e., the charges are released by the trap at a rate which is much faster than those expected from the equation and the phenomenon is only weakly dependent on the temperature. This kind of fading is known as anomalous fading and it is explained by **tunnelling** of carriers from the trap to the recombination centre [1,2].

The anomalous fading is observed in natural minerals, as well as in TL materials as ZnS:Cu, ZnS:Co, CaF₂:Mn, KCl:Tl, etc.

The characteristic of the anomalous fading is an initial rapid decay followed by a decrease of the decay rate over long storage periods.

The experimental way for detecting a suspected anomalous fading is to perform a long-term fading experiment in order to accumulate a measurable signal loss and to compare the experimental amount of fading to the one calculated taking into account the quantities E , s and the storage temperature.

References

1. McKeever S.W.S., Thermoluminescence of Solids, Cambridge University Press (1985)
2. Chen R. and Kirsh Y., Analysis of Thermally Stimulated Processes, Pergamon Press (1981)

Anomalous thermal fading

This effect has been encountered in dating of meteorites. When very long periods of storage/irradiation are involved, a thermal fading of the TL corresponding to very deep traps becomes significant. This means that the thermal detrapping of these traps takes place at the same time of their filling due to the irradiation. In case of very long periods it can be possible to reach an equilibrium condition between the filling rate and the detrapping rate although a saturation level has not reached.

Area measurement methods (generality)

The area methods are based on the measurements of the integral of the glow-peak; it can be applied when a well isolated and clean peak is available.

Assuming a first order kinetics, the Randall-Wilkins relation in the time domain gives

$$\int_{t_0}^t I dt = n = \frac{I}{s \exp(-\frac{E}{kT})} \quad (1)$$

In the temperature domain the same relation leads to

$$\frac{I}{\int_T^{T_\infty} I dT} = \frac{s}{\beta} \exp(-\frac{E}{kT}) \quad (2)$$

$$\ln\left[\frac{I}{\int_T^{T_\infty} I dT}\right] = \ln\frac{s}{\beta} - \frac{E}{kT} \quad (3)$$

where the integral is calculated as shown in Fig. 1.

Again, the \ln term is a linear function of $1/T$ and can be plotted on a semilog paper to obtain the slope $-E/k$ and the intercept $\ln(s/\beta)$.

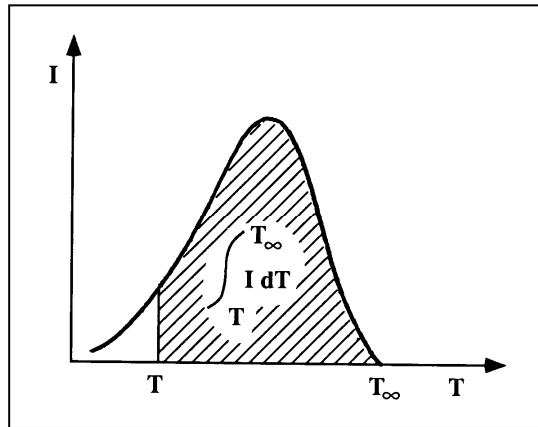


Fig. 1. How to calculate the integral comparing in Eq. (3).

Area measurement method (Maxia et al.)

Maxia et al. [1] have suggested a rather complicated area method for the evaluation of both activation energy and frequency factor. It essentially stems from the fact that the filled traps density, at any temperature T , is proportional to the remaining area of the

glow-peak. The main assumption is that the various peaks in a complex glow-curve result from the escape of electrons from a single trap and their recombination into various recombination centres. The mathematical treatment is based on the equation proposed by **Antonov-Romanovskii** [2]:

$$\frac{dm_i}{dt} = -s \exp\left(-\frac{E}{kT}\right) \frac{B_i n m_i}{A(N-n) + B_i m_i} \quad (1)$$

where, in particular

- m_i is the concentration of luminescent centers,
- A is the probability factor for retrapping,
- B_i is the probability for recombination,
- N is the electron trap concentration,
- n is the trapped electron concentration.

Using a constant heating rate one can write

$$\frac{dm_i}{dT} = \alpha I(T) \quad (2)$$

where α being a constant depending on the light collection efficiency and the used units.

From Eq. (2) one has

$$m_i(T) = \alpha \int_T^{T_f} I(T') dT' = \alpha S(T) \quad (3)$$

and

$$m_{i0} = \alpha \int_{T_0}^{T_f} I(T') dT' = \alpha S_0 \quad (4)$$

in which

T_0 = temperature at beginning of the glow-peak,

T_f = temperature at the end of the glow-peak,

T = temperature between T_0 and T_f ,

S_0 = total area from T_0 to T_f ,

S = area from T and T_f .

Introducing now the areas σ and Σ defined as

$$n_0 = \alpha \sigma \quad (5)$$

$$N = \alpha \Sigma \quad (6)$$

from a single glow-peak one obtains

$$n_0 = m_{i0} \quad (7)$$

and then

$$\sigma = S_0 \quad (8)$$

where n_0 and m_{i0} represent initial values.

By straight-forward calculations, using Eq. (1) to Eq. (6), one gets

$$\ln \left[I(T) \frac{\cos \theta + S(T) \sin \theta}{S^2(T) + S(T)\Delta} \right] = -\frac{E}{kT} + \mu \quad (9)$$

where

$$\tan \theta = \frac{B - A}{A(\Sigma - \sigma + S_0)} \quad (10)$$

$$\Delta = \sigma - S_0 \quad (11)$$

$$\mu = -\frac{1}{2} \ln \left\{ \left(\frac{\beta}{Bs} \right)^2 \left[A^2 (\Sigma - \sigma + S_0)^2 + (B - A)^2 \right] \right\} \quad (12)$$

The plot of Eq. (9) will be rectilinear if an appropriate value of θ is chosen. The angle θ depends on unknown parameters, as one can see from Eq. (10). To determine θ one can put

$$y = \ln \left[I(T) \frac{\cos \theta + S(T) \sin \theta}{S^2(T) + S(T)\Delta} \right] \quad (13)$$

$$x = \frac{1}{T} \quad (14)$$

The searched value for θ is the one corresponding to a linear behaviour of y versus x . Such a behaviour can be carried out considering the covariance, $\text{cov}(x, y)$, and the variances, $v(x)$ and $v(y)$, for x and y respectively. In this way the correlation coefficient can be numerically computed as a function of θ . Then, using the angular coefficient of the straight line described by Eq. (9), the activation energy can be found as

$$E = -k \frac{\text{cov}(x, y)}{v(x)} = -k \frac{\text{cov}(x, y)}{v(y)} \quad (15)$$

The Authors claim that this method is also applicable when overlapped peaks are present.

References

1. Maxia V., Onnis S. and Rucci A., *J. Lum.* **3** (1971) 378
2. Antonov-Romanovskii V.V., *Isvest. Akad. Nauk. SSSR Fiz.* **10** (1946) 477

Area measurement methods (May and Partridge: general order)

May and Partridge proposed the **area method** in the case of a general order b is considered. In this case the equation is

$$\ln\left(\frac{I}{n^b}\right) = \ln(s) - \frac{E}{kT} \quad (1)$$

which is graphically processed in the usual way. By visual examination of such plots, the value of b which gives the best straight line can be ascertained.

Reference

May C.E. and Partridge J.A., *J. Chem. Phys.* **40** (1964) 1401

Area measurement methods (Muntoni et al.: general order)

Muntoni and co-workers suggested a method base on the glow prak area and on the fact that the filled traps density, at any temperature T , is proportional to the remaining area of the glow-peak $S(T)$. They used the general order kinetics equation in the form

$$I = -a \frac{dm}{dt} = aAm^b \exp\left(-\frac{E}{kT}\right) \quad (1)$$

where m is the concentration of recombination centres, A is a proportionality factor, b represents the kinetic order and a is a constant. The integral area, $S(T)$ in the interval from T to T_f in the glow-curve, is given by

$$S(T) = \int_T^{T_f} IdT = -a\beta \int_m^0 dm = a\beta m \quad (2)$$

from which, considering the order b ,

$$m^b = \left[\frac{S(T)}{a\beta} \right]^b \quad (3)$$

Equation (1), using Eq. (3), yields to

$$\ln \frac{I}{[S(T)]^b} = c - \frac{E}{kT} \quad (4)$$

A plot of the first term against $1/T$ gives a straight line when the best value for b is chosen.

Reference

Muntoni C., Rucci A. and Serpi A., Ric. Sci. **38** (1968) 762

Area measurement method (Moharil: general order)

This method [1] uses the peak area and it is based on the **Antonov-Romanovskii equation** [2]:

$$I = -\frac{dn}{dt} = s \frac{Bnm}{Bn + A(N - n)} \exp\left(-\frac{E}{kT}\right) \quad (1)$$

Considering that:

n_0 is proportional to the area under the total peak ($= A_0$); n is proportional to the remaining area, A_T , under the glow peak, from a given temperature T to the end of the peak. If $n_0 = N$, saturation case, A_0 is proportional to N : in this case the area is denoted A_S instead of A_0

Eq. (1) transforms in, with the conditions $n = m$, $n = n_0$

$$I = \frac{BA_T^2}{(B - A)A_T + AA_S} s \exp\left(-\frac{E}{kT}\right) \quad (2)$$

Considering the intensity at the maximum, I_M , and the half maximum intensities, I_1 and I_2 , from Eq. (2) can be derived the following two expressions:

$$\begin{aligned} \ln 2 &= -\frac{E}{k} \left(\frac{1}{T_M} - \frac{1}{T_2} \right) + \ln \left(\frac{A_{T_M}^2}{A_{T_2}^2} \cdot \frac{A_{T_2} + (A_S - A_{T_2}) \frac{A}{B}}{A_{T_M} + (A_S - A_{T_M}) \frac{A}{B}} \right) \\ \ln 2 &= +\frac{E}{k} \left(\frac{1}{T_1} - \frac{1}{T_M} \right) - \ln \left(\frac{A_{T_1}^2}{A_{T_M}^2} \cdot \frac{A_{T_M} + (A_S - A_{T_M}) \frac{A}{B}}{A_{T_1} + (A_S - A_{T_1}) \frac{A}{B}} \right) \end{aligned} \quad (3)$$

For different values of the ratio A/B , E can be calculated. The correct value of A/B is the one which gives the same value of E from both equations.

The same procedure can be carried out in the case of non-saturation doses [3].

References

1. Moharil S.V., Phys. Stat. Sol. (a) **73** (1982) 509
2. Atonov-Romanoski V.V., Bull. Acad. Sci. USSR Phys. Res. **15** (1951) 673
3. Moharil S.V. and Kathurian S.P., J. Phys. D: Appl. Phys. **16** (1983) 2017

Area measurement method (Moharil: general order, $s = s(T)$)

Moharil suggested a new method to obtain the trapping parameters which does not require a priori knowledge of the order of kinetics. Furthermore, he assumes a temperature dependence of the frequency factor.

Starting from the general order equation, he modifies it as following, taking into account the temperature dependence of the frequency factor:

$$I = -\frac{dn}{dt} = s_0 T^\alpha n^b \exp\left(-\frac{E}{kT}\right) \quad (1)$$

and assumes that the glow-curve consists of a single glow-peak corresponding to traps of only one kind.

If it is assumed that at the end of the glow-curve all the traps are emptied, the number of traps populated at the beginning of the glow-curve, n_0 , is proportional to the area under the glow-curve. As a consequence, the number of traps emptied up to the temperature T is given by the area under the glow-curve up to T . Hence, the number of populated traps at temperature T is proportional to the area A_T which is equal to the total area under the glow-curve less the area under the curve between the initial point and T . So, Eq. (1) becomes

$$I = B s_0 T^\alpha A_T^b \exp\left(-\frac{E}{kT}\right) \quad (2)$$

where B is a constant.

Let us say T_M be the temperature at which the TL intensity is maximum and T_1 and T_2 be the temperatures at which the intensity falls to half of its maximum both on the low and high temperature sides of T_M , respectively. Fig. 1 shows the different parameters. Equation (2) gives then

$$\begin{aligned}
 I_M &= B s_0 T_M^\alpha A_{T_M}^b \exp\left(-\frac{E}{kT_M}\right) \\
 I_1 &= \frac{I_M}{2} B s_0 T_1^\alpha A_{T_1}^b \exp\left(-\frac{E}{kT_1}\right) \\
 I_2 &= \frac{I_M}{2} B s_0 T_2^\alpha A_{T_2}^b \exp\left(-\frac{E}{kT_2}\right)
 \end{aligned} \tag{3}$$

From the previous expressions one obtains

$$\begin{aligned}
 \ln 2 &= -\alpha \ln\left(\frac{T_2}{T_M}\right) + b \ln\left(\frac{A_{T_M}}{A_{T_2}}\right) - \frac{E}{k} \left(\frac{1}{T_M} - \frac{1}{T_2}\right) \\
 \ln 2 &= -\alpha \ln\left(\frac{T_M}{T_1}\right) + b \ln\left(\frac{A_{T_1}}{A_{T_M}}\right) - \frac{E}{k} \left(\frac{1}{T_1} - \frac{1}{T_M}\right)
 \end{aligned} \tag{4}$$

The terms containing α can be neglected because $\ln(T_2/T_M)$ and $\ln(T_M/T_1)$ are of the order of 10^{-2} and α lies between -2 and +2. Using Eq. (4) E and b can then be obtained. The value of α is obtained by Eq. (2):

$$\ln I = \ln B + \alpha \ln T + b \ln A_T - \frac{E}{kT} \tag{5}$$

Because at $T=T_M$, $d(\ln I)/dT=0$, one gets

$$\alpha = -\left(b T_M \frac{d}{dT} (\ln A_T)_{T=T_M} \right) - \frac{E}{kT_M} \tag{6}$$

where $d(\ln A_T)/dT$ is known experimentally and will be negative. The sign of α depends upon whether E/kT_M is larger or smaller than $\left[b T_M d(\ln A_T)/dT \right]_{T=T_M}$.

After having determined the values of α , b and E , one can now obtain the frequency factor starting from the **general order equation including the temperature dependence of the frequency factor**:

$$-\frac{dn}{dt} = -n^b s_0 T^\alpha \exp\left(-\frac{E}{kT}\right) \tag{7}$$

which can be written as, using a linear heating rate $\beta = \frac{dT}{dt}$

$$-\frac{dn}{n^b} = \frac{s_0}{\beta} T^\alpha \exp\left(-\frac{E}{kT}\right) dT \tag{8}$$

Integrating this equation between 0 and T and using the condition $n = n_0$ at $T = 0$:

$$\int_{n_0}^n \frac{dn}{n^b} = -\frac{s_0}{\beta} \int_0^T T^\alpha \exp\left(-\frac{E}{kT'}\right) dT'$$

$$n^{1-b} = n_0^{1-b} - \frac{s_0(1-b)}{\beta} \int_0^T T^\alpha \exp\left(-\frac{E}{kT'}\right) dT'$$

and the expression of n is obtained:

$$n = n_0 \left[1 + \frac{s_0 n_0^{b-1} (b-1)}{\beta} \int_0^T T^\alpha \exp\left(-\frac{E}{kT'}\right) dT' \right]^{\frac{1}{1-b}} \tag{9}$$

so that the expression of the intensity I is now

$$I = n_0^b s_0 T^\alpha \exp\left(-\frac{E}{kT}\right) \left[1 + \frac{(b-1) s_0 n_0^{b-1}}{\beta} \int_0^T T^\alpha \exp\left(-\frac{E}{kT'}\right) dT' \right]^{\frac{b}{b-1}}$$

where $s_0 n_0^{b-1} T^\alpha$ is similar to the frequency factor s of the first-order equation.

Using the substitution

$$RT^\alpha = s \quad \text{with} \quad R = s_0 n_0^{b-1}$$

the previous equation for the intensity becomes

$$I = n_0 R T^\alpha \exp\left(-\frac{E}{kT}\right) \left[1 + \frac{(b-1)R}{\beta} \int_0^T T^\alpha \exp\left(-\frac{E}{kT'}\right) dT' \right]^{\frac{b}{b-1}} \tag{10}$$

Because $dI/dT = 0$ at $T = T_M$, Eq. (10) gives

$$R = \frac{\alpha + \frac{E}{kT_M}}{\left(\frac{b}{\beta}\right) T_M^{\alpha+1} \exp\left(-\frac{E}{kT_M}\right) - \left(\alpha + \frac{E}{kT_M}\right) \left[\frac{b-1}{\beta}\right] \int_0^T T^\alpha \exp\left(-\frac{E}{kT'}\right) dT'} \quad (11)$$

where the integral is evaluated by graphical method or using the Newton-Raphson method. The frequency factor at any temperature is then calculated by $s=RT^a$.

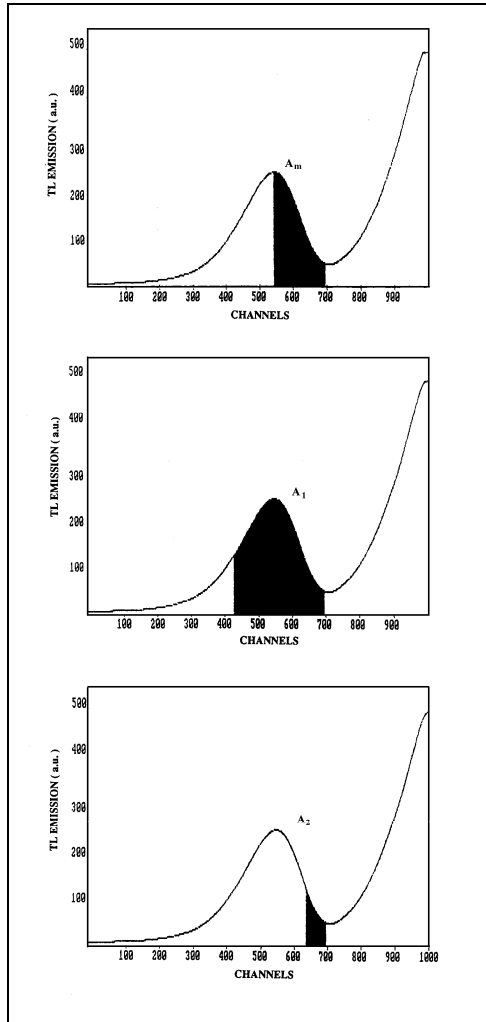


Fig. 1. In this figure the channel number is proportional to the temperature.

Reference

Moharil S.V., Phys. Stat. Sol. (a) **66** (1981) 767

Area measurement method (Rasheedy: general order)

M.S. Rasheedy developed a method for obtaining the trap parameters of a complex TL glow-curve including several peaks [1]. His method is based on a development of **Moharil's method**. The trap parameters are obtained starting from the higher temperature glow peak. The procedure begins by determining the order of kinetics, b , of the higher temperature peak of the glow curve.

It is assumed, at first, that the glow curve consists in a single glow-peak, corresponding to only one kind of traps. Furthermore, it is also assumed that all the traps are emptied at the end of the glow-curve. As usual, the concentration of the trapped charges, at the beginning of the glow-curve, n_0 , is proportional to the area A under the glow-curve; then, the concentration of trapped charges at any temperature T_i , during the read out run, is proportional to the area A_i under the glow-curve between T_i and the final temperature, T_f , at which the TL light falls to zero. Fig. 1 gives a sketch of an isolated peak with indication of the different parameters.

Taking into account the equation for a general order kinetics written as following [2]:

$$I = -\frac{dn}{dt} = \frac{n^b}{N^{b-1}} s \exp\left(-\frac{E}{kT}\right) \quad (1)$$

and considering the maximum intensity of the peak, I_M , the previous equation becomes

$$I_m = \frac{A_m^b}{N^{b-1}} s \exp\left(-\frac{E}{kT_m}\right) \quad (2)$$

According to the quantities shown in Fig. 1, the following equations can also be written

$$\begin{aligned} I_2 = \frac{I_M}{2} &= \frac{A_2^b}{N^{b-1}} s \exp\left(-\frac{E}{kT_2}\right) \\ I_4 = \frac{I_M}{4} &= \frac{A_4^b}{N^{b-1}} s \exp\left(-\frac{E}{kT_4}\right) \end{aligned} \quad (3)$$

where A_2 and A_4 are the areas under the glow peak from T_2 to T_f and from T_4 to T_f respectively.

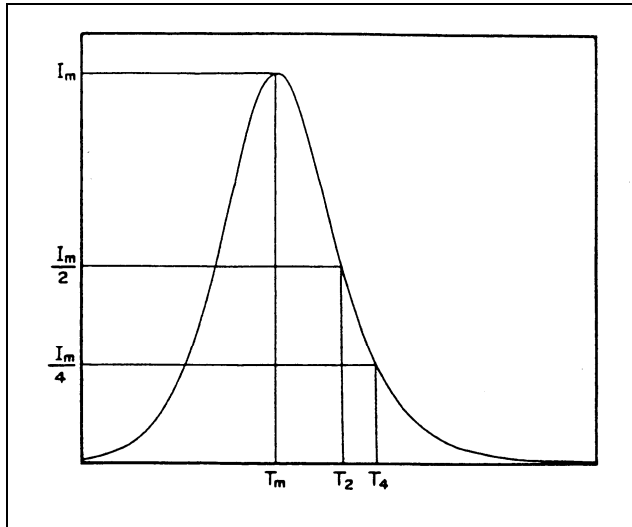


Fig. 1. An isolated glow-peak with the parameters of interest.

Making now the logarithm of Eqs. (2) and (3) one gets

$$E = \frac{[\ln 2 - b \ln(\frac{A_M}{A_2})]kT_M T_2}{T_M - T_2} \quad (4)$$

$$E = \frac{[\ln 2 - b \ln(\frac{A_M}{A_4})]kT_M T_4}{T_M - T_4} \quad (5)$$

Eliminating E from the two previous equations, it is easy to find an expression which gives the kinetics order b :

$$b = \frac{T_2(T_M - T_4) \ln 2 - T_4(T_M - T_2) \ln 4}{T_2(T_M - T_4) \ln(\frac{A_M}{A_2}) - T_4(T_M - T_2) \ln(\frac{A_M}{A_4})} \quad (6)$$

The previous equations can be arranged to determine E and b using any portion of the descending part of the glow-peak. Let us indicate I_x the TL intensity at a temperature T_x of the descending part of the peak and T'_2 and T'_4 the temperatures at which the TL intensities are equal to $I_x/2$ and $I_x/4$ respectively; the new equations are then

$$E = \frac{[\ln 2 - b \ln(\frac{A_x}{A_2})]kT_x T_2'}{T_x - T_2'}$$

$$E = \frac{[\ln 2 - b \ln(\frac{A_x}{A_4})]kT_x T_2'}{T_x - T_4'} \tag{7}$$

$$b = \frac{T_2'(T_x - T_4') \ln 2 - T_4'(T_x - T_2') \ln 4}{T_2'(T_x - T_4') \ln(\frac{A_M}{A_2}) - T_4'(T_x - T_2') \ln(\frac{A_x}{A_4})} \tag{8}$$

The same method is then applied to glow-curves having peaks more than one. In particular, the Author applies his method to BeO which presents a glow-curve with two well resolved peaks. The first step of the method consists in determining the trap parameters of the higher temperature peak. The value of b of the peak is evaluated at different intensities of the descending part of the peak starting from T_M . The pre-exponential factor

$$s'' = s(\frac{n_0}{N})^{b-1} \tag{9}$$

and the relative value n_0 are estimated by the equation

$$S'' = \frac{\beta E \exp(\frac{E}{kT_M})}{bkT_M^2 - E(b-1)\Phi \exp(\frac{E}{kT_M})} \tag{10}$$

and where

$$\Phi = \int_{T_0}^{T_M} \exp(-\frac{E}{kT'})dT'$$

Eq. (10) is obtained by equating the derivative of the following equation to zero

$$I(T) = n_0 s'' \exp\left(-\frac{E}{kT}\right) \left[1 + \frac{s''(b-1)}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{kT'}\right) dT' \right]^{\frac{1}{1-b}} \tag{11}$$

Now, substituting s'' in Eq. (11) one obtains

$$I = \frac{n_0 s'' \exp\left(-\frac{E}{kT_M}\right)}{\left\{1 + \left[\frac{(b-1)s''}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{kT'}\right) dT'\right]^{\frac{b}{b-1}}\right\}} \quad (12)$$

Furthermore, the relative value of n_0 can be found using the maximum intensity I_M . In this case the procedure is the usual one, which means to make the logarithm of Eq. (11), then its derivative respect to the temperature T and finally to equate to zero the derivative at $T = T_M$. In this way the maximum of the intensity, I_M , is given by the following expression:

$$I_M = \frac{n_0 s'' \exp\left(-\frac{E}{kT_M}\right)}{\left[\frac{kT_M^2 b s''}{\beta E} \exp\left(-\frac{E}{kT_M}\right)\right]^{\frac{b}{b-1}}} \quad (13)$$

from which the value of n_0 is obtained

$$n_0 = \frac{I_M \exp\left(\frac{E}{kT_M}\right)}{s''} \left[\frac{b k T_M^2 s''}{\beta E \exp\left(\frac{E}{kT_M}\right)} \right]^{\frac{b}{b-1}} \quad (14)$$

Reference

1. Rasheedy M.S., J. Phys. D: Appl. Phys. **29** (1996) 1340
2. Rasheedy M.S., J. Phys.: Condens. Matter. **5** (1993) 633

Arrhenius equation

The Arrhenius equation gives the mean time, τ , that an electron spends in a trap at a given temperature T . It is

$$\tau = s^{-1} \exp\left(\frac{E}{kT}\right) \quad (1)$$

where s is the frequency factor (in the case of thermoluminescence the frequency factor is also called attempt-to-escape frequency), E is the energy difference between the bottom

of the CB and the trap position in the band gap, also called trap depth or activation energy, k is the Boltzmann's constant.

Eq. (1) can be rewritten as

$$p = \tau^{-1} \quad (2)$$

which gives the probability p , per unit of time, of the release of an electron from the trap.

According to Eq. (1), if the trap depth is such that at the temperature of irradiation, let us say T_i , E results to be much larger than kT_i , electrons produced by irradiation and then trapped will remain in the trap for a long period of time, even after the removal of the irradiation. The Arrhenius equation introduces the concept of an **activation energy**, E , seen as an energy barrier which must be overcome in order to reach equilibrium.

Reference

Bube R.H., Photoconductivity of Solids, Wiley & Sons, N.Y. (1960)

Assessment of random uncertainties in precision of TL measurements (general)

The reproducibility of TL measurements depends on the dose level. The following Fig. 1 shows how the standard deviation, in percentage, behaves as a function of the dose.

From the figure it can be observed that the relative standard deviation in percentage decreases very fast as the dose increase. As the dose increases, the relative standard deviation assumes a minimum constant value.

This behaviour is justified by the competition of two components:

- the intrinsic variability of the TL system, given by the standard deviation of the zero dose readings (background),
- the variation of the TL system at high doses, expressed in terms of standard deviation.

Burkhardt and Piesh [1] and Zarand and Polgar [2,3] used a mathematical formalism to describe the effect of the two components so far introduced. They proposed the following expression

$$\sigma_D = \sqrt{\sigma_{BKG}^2 + \sigma_{r,D}^2 D^2} \quad (1)$$

where

σ_D = standard deviation of the evaluated dose D ,

σ_{BKG} = standard deviation of the zero-dose readings, expressed in unit of dose,

$\sigma_{r,D}$ = relative standard deviation of the readings obtained at the dose D , relatively high.

Eq. (1) can be re-written as

$$\frac{\sigma_D}{D} = \sqrt{\frac{\sigma_{BKG}^2}{D^2} + \sigma_{r,D}^2} \quad (2)$$

From Eq. (2) it can be observed that:

- the ratio σ_{BKG}/D becomes almost zero for doses quite large respect to σ_{BKG} and then $\sigma_D/D \approx \sigma_{r,D}$, which takes into account of the minimum and constant value observed,
- for very little doses, the term $\sigma_{r,D}$ becomes negligible and the Eq. (2) assumes the form

$$y = \frac{a}{x} \quad (3)$$

- expression (3), on a log-log scale, is a straight line having a unity negative slope (in the region 1 – 10 μGy of the Fig. 2).
- furthermore, modifying Eq. (2) as in the following

$$\frac{\sigma_D}{D} = \sqrt{\left(\frac{\frac{\sigma_{BKG}}{D}}{\sigma_{BKG}} \right)^2 + \sigma_{r,D}^2}$$

or better

$$\frac{\sigma_D}{D} = \sqrt{\frac{1}{R^2} + B^2} \quad (4)$$

From Eq. (4) results that σ_D/D is independent by the standard deviation, expressed in terms of dose, of the zero-dose readings, but only depends by R and $\sigma_{r,D}$, as it is shown in Fig. 3

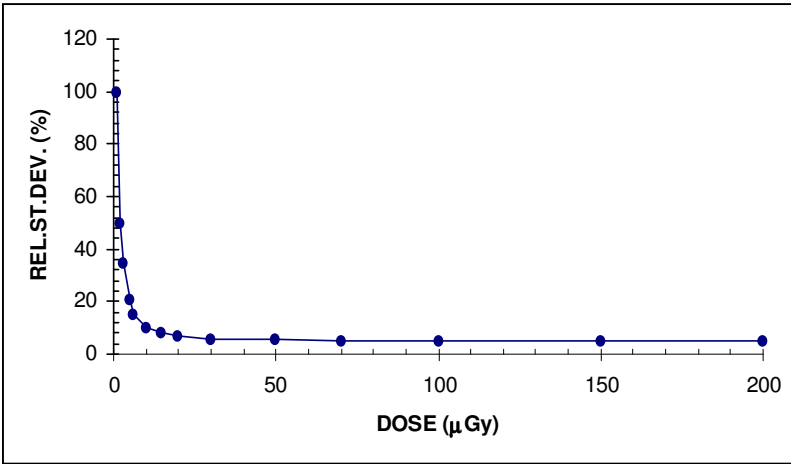


Fig. 1. Behaviour of the Rel. Stand. Dev. of the TL readings as a function of dose.

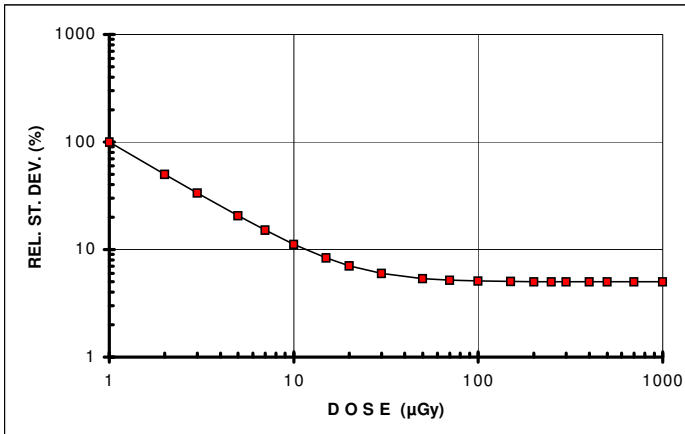


Fig. 2. Same plot of Fig. 1 but in log-log scale.

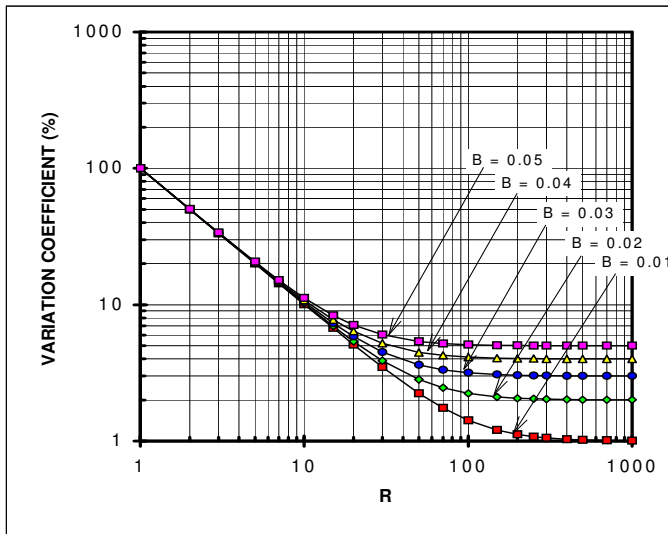


Fig. 3. Behaviour of $\frac{\sigma_D}{D}(\%)$ as a function of $R = \frac{D}{\sigma_{BKG}}$
for given values of $B = \sigma_{r,D}$.

References

1. Burkhardt B. and Piesh E., Nucl. Instr. Meth. **175** (1980) 159
2. Zarand P. and Polgar I., Nucl. Instr. Meth. **205** (1983) 525
3. Zarand P. and Polgar I., Nucl. Instr. Meth. **222** (1984) 567

Atomic number (calculation)

For some practical dosimetric applications, as the wide range of radiological dosimetry, two properties of the TL dosimeters are advantageous for precise measurements. These are high sensitivity and tissue equivalence. High sensitivity thermoluminescent phosphors (i.e. CaF_2 and CaSO_4) have high effective atomic numbers, Z_{eff} , so that at photon energies below about 100 keV, the response to a given absorbed dose of radiation becomes significantly greater than that at higher energies. In this region the photoelectric effect is predominant and the cross section per atom depends upon approximately Z^4 for high atomic number materials and on $Z^{4.8}$ for low Z materials. Since each atom contains Z electrons, the coefficient per electron depends upon Z^3 and $Z^{3.8}$ for high and low Z materials respectively.

It is important to know a priori the effective atomic number of a thermoluminescent material, Z , for getting an approximated idea of the expected TL response at different energies. The behaviour of different materials to X and gamma rays

depends on the atomic number of the constituents and not on the chemical composition of these constituents.

$$\bar{Z} = \sqrt[x]{a_1 Z_1^x + a_2 Z_2^x + \dots} \quad (1)$$

$$a_i = \frac{n_i(Z_i)}{\sum_i n_i(Z_i)} \quad (2)$$

$$n_i = N_A \cdot Z_i \quad (3)$$

where a_1, a_2, \dots are the fractional contents of electrons belonging to elements Z_1, Z_2, \dots respectively, n_i is the number of electrons, in one mole, belonging to each element Z_i and N_A is the Avogadro's number. The value of x is 2.94.

A numerical example concerning LiF is given below:

1 mole of compounds contains $6.022 \cdot 10^{23}$ atoms so that 1 mole of LiF has $6.022 \cdot 10^{23}$ atoms of Li and $6.022 \cdot 10^{23}$ atoms of F. Now, the number of electrons belonging to each element in 1 mole of compound is given by the atomic number of the element multiplied by the number of atoms:

$$\begin{aligned} \text{for Li: } & 3 \cdot 6.022 \cdot 10^{23} = 1.81 \cdot 10^{24} \text{ electrons,} \\ \text{for F: } & 9 \cdot 6.022 \cdot 10^{23} = 5.41 \cdot 10^{24} \text{ electrons.} \end{aligned}$$

The total amount of electrons in LiF is then $7.23 \cdot 10^{24}$.

The partial contents, a_i , are respectively

$$\begin{aligned} a_{Li} &= \frac{1.81 \cdot 10^{24}}{7.23 \cdot 10^{24}} = 0.25 \\ a_F &= \frac{5.41 \cdot 10^{24}}{7.23 \cdot 10^{24}} = 0.75 \end{aligned}$$

Then

$$\begin{aligned} Z_{Li}^{2.94} &= 3^{2.94} = 25.28 \\ Z_F^{2.94} &= 9^{2.94} = 638.96 \end{aligned}$$

from which

$$\begin{aligned} a_{Li} \cdot Z_{Li}^{2.94} &= 6.32 \\ a_F \cdot Z_F^{2.94} &= 479.22 \end{aligned}$$

and finally

$$\bar{Z} \approx 8.2$$

Alternatively, the number of electrons per gram can be calculated as follows

$$n_i = \left(\frac{N_A \cdot Z_i}{A_{w,i}} \right) \cdot W_i \quad (4)$$

where N_A is the Avogadro's number, $A_{w,i}$ is the atomic number, W_i is the fractional weight and Z_i is the atomic number of the i -th element in the compound.

The following table shows the atomic number of the main TL materials.

phosphors	effective atomic number
LiF:Mg,Ti LiF:Mg,Ti,Na LiF:Mg,Cu,P	8.14
Li ₂ B ₄ O ₇ :Mn Li ₂ B ₄ O ₇ :Cu Li ₂ B ₄ O ₇ :Cu,Ag	7.4
MgB ₄ O ₇ :Tm MgB ₄ O ₇ :Tb	8.4
CaSO ₄ :Dy CaSO ₄ :Tm CaSO ₄ :Mn	15.3
CaF ₂ :Dy CaF ₂ :Mn CaF ₂ (nat) CaF ₂ :Tm	16.3
BeO	7.13
Al ₂ O ₃	10.2
ZrO ₂	35.6
KMgF ₃ (various activators)	13.4
CVD diamond	6
Ca ₅ F(PO ₄) ₃	14
MgF ₂	10
Mg ₂ SiO ₄	11
Na ₄ P ₂ O ₇	11

Reference

Mayneord W.V., The significance of the Roentgen. Acta Int. Union Against Cancer **2** (1937) 271