A METHOD FOR ADJUSTING TEMPERATURE-TIME
FADING CHARACTERISTICS IN TL PHOSPHORS:
APPLICATIONS IN WIDE RANGE THERMAL DOSE MONITORING

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Abstract: Thermal fading of TL Phosphors can be used to monitor thermal dose over some temperature-time range. For practical use the TL activation energy must be matched to the temperature-time characteristic desired. Simple criteria can be derived to establish the approximate glow peak peaking temperature, T_m , necessary to ensure the appropriate effective activation energy. We describe how the complex, composite, glow curves of many common TL phosphors can be modified substantially by controlling the initial radiation dose, its quality, and by varying initial pre-annealing. This enables one to adjust T_m to any desired value over a reasonably wide range.

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Introduction. Thermal dose measurements are a recognized and growing need

In many areas of industrial, environmental, and research activities. Applications range from the thermal monitoring of large commercial food storage and shipment refrigeration plans to the thermal charting of fish migration patterns between the cold intake waters and warm outflow waters of lake-front situated power plants. For limited use, spot checking, operations thermometry with actively powered recording apparatus can be used in some circumstances; however, for wide spread routine, or long term unattended applications active device thermal dosimetry is too expensive and unreliable. In these circumstances, one needs a simple, inexpensive, reliable, tamper proof, passive thermal dosimeter. These requirements are met by the thermal fading properties of thermoluminescence phosphors. The TL fading technique for thermal dosimetry has been used in some specific applications; the practical problem blocking a more widespread utilization of these techniques is that for a particular temperature-time dose to be monitored one must find or develop a new TL phosphor of appropriate characteristics. This paper describes how one can utilize a few well known TL phosphors for thermal dose monitoring over a very wide range of temperature-time requirements; by varying the initial sensitizing ionizing radiation exposure both in quality and in dose together with a post irradiation range of desired temperature-time decay characteristics.

We provide first a brief review of the behavior of ordinary thermoluminescence dosimetry phosphors, then describe how these are used in thermal dose monitoring and develop criteria for optimal temperature-time fading characteristics for a given application, then present experimental data on two common TL materials, CaF_2 and $\text{CaSO}_4:\text{Mn}$, and finally present

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a brief phenomenological theory which describes the physical basis for the method of varying fading characteristics of a given phosphor and guides the selection of irradiation and thermal annealing procedures for a desired thermal dose monitoring application.

Simple thermoluminescence systems. When an otherwise insulating solid is exposed to ionizing radiation or photoconductivity-inducing light, mobile electrical charges, both electrons and holes (negative and positive charges), are produced transiently. Some of these charges recombine with their oppositely charged counterpart, but some of them become trapped into highly immobile states in the dielectric solid. The trapping centers may be either native or impurity-related defect states in the solid or, in some cases, the trapping sites may be self generated by the presence of the mobile charge (e.g., the self-trapped hole or V_K -center in the alkali or alkaline earth halides). Any ambient thermal energy, however, will to some extent remobilize these metastably trapped charges; at low temperatures the degree of thermal remobilization can be so low that thousands of years are required for the trapped charge concentration to show any significant decrease. At higher temperatures, on the other hand, the thermal remobilization can be so strong that the trapped charge concentration fades to undetectable levels within a few seconds. These thermally mobilized charges disappear either through recombination or through retrapping at other defect centers of even greater binding energy. If the recombination or retrapping centers are optically active, then the initially metastably trapped charge disappears with some probability for emitting light; the total amount of light emitted can be measured, for example, by a sensitive photomultiplier during a readout thermal scan of the phosphor subsequent to irradiation. The light output is a quantitative indicator of the total

concentration of metastably trapped charge at the initiation of the readout scan. This trapped charge concentration, in turn, is related to both the initial radiation exposure and to the degree of thermal remobilization which occurred in the interval between the initial radiation of the phosphor and its subsequent readout; this loss is called the thermal fading of the material. Related to the thermoluminescence (TL) effect described above is the thermocurrent (TC) effect; during the readout temperature scan, the highly remobilized charges can be detected directly as a transient electrical current. Recent experiments at the laboratory have shown that the TC effect in certain highly purified materials is even more sensitive in detection than the TL phenomena; TC effects could be equally as applicable in thermal dose monitoring as TL effects, but in the present paper we describe explicitly only the more well-known phenomenon.

A typical simple TL system readout is indicated in Fig. 1. This is an actual tracing from a TL readout (thermogram) of UV-grade calcium fluoride purchased from the Harshaw Chemical Corporation. This sample was exposed to ultraviolet light from a high pressure mercury arc at 77° K; subsequently the sample was heated for readout at a linear temperature scan of 1°K sec^{-1} . Figure 1 shows the characteristic TL light intensity thermogram during readout; the glow curve peaks at a characteristic temperature, T_m , which in this case is 298°K, and T_m is a useful descriptor of the TL thermogram as it depends only weakly upon the temperature scan rate, a small logarithmic dependence, but depends directly upon the particular microscopic trapping center properties. The temperature breadth at half maximum of the thermogram is approximately 30°K; this thermal half breadth is also characteristic of the particular TL system. In most simple systems the ratio of the thermal half breadth,

ΔT to T_m is approximately 0.1 for reasons we shall describe later.

At given temperature the decay of the trap charge concentration, n , for the simple systems we are considering is described by

$$d_t n = W(T) n \quad (1)$$

where " d_t " is the time derivative operation and $W(T)$ is the decay rate at absolute temperature T . The TL emission rate, ϕ , depends on the recombination or retrapping rate, so that

$$\phi = \epsilon (d_t n) \quad (2)$$

where ϵ is a nearly temperature independent optical emission efficiency.

The total light output during readout, $L(t_R)$, is the integrated light intensity from the time of readout, t_R , to the end of the readout cycle which for convenience we denote as " ∞ ", and

$$L(t_R) = \int_{t_R}^{\infty} \phi(t') dt' \quad (3)$$

from which Eq. 2 yields

$$L_R \equiv L(t_R) = \epsilon n(t_R) \quad (4)$$

We denote the time at the end radiation exposure and any annealing procedures by t_0 ; thus we may write from Eq. 4

$$L_0 \equiv L(t_0) = \epsilon n(t_0) \equiv \epsilon n_0 \quad (5)$$

Suppose now that one irradiates a sample, perhaps followed by an annealing procedure, and immediately performs a TL readout; this yields a quantitative value for L_0 . One may then perform an identical irradiation-annealing procedure, but allow the sample to fade within some desired temperature-time interval; following this, one measures the remaining TL output to obtain L_R and one may take the ratio of the two light outputs to obtain

$$L_R L_0^{-1} = n(t_R) n_0^{-1} \quad (6)$$

Let us call the intervening thermal dose interval, $t_R - t_0 = t_d$; the formal solution of Eq. 1 gives

$$n(t_R) n_0^{-1} = \exp\left\{-\int_{t_0}^{t_R} W(T) dt\right\}, \quad (7)$$

in which T is an implicit function of time during the thermal dose interval $t_R - t_0$. For descriptive simplicity we assume temporarily that the temperature is constant during t_d ; then Eq. 7 may be written

$$L_R L_0^{-1} = n(t_R) n_0^{-1} = \exp\{-W(T) t_d\}. \quad (8)$$

Equation 8 describes the thermal dose measuring method; if $W(T)$ is a known function of temperature and the dose interval t_d is known then the logarithm of the light ratios $(L_R/L_0)^{-1}$ can be used together with Eq. 8 for computing the effective thermal dose temperature during the interval in question.

The idea is straight forward, but even for the simple system described above practical utilization is not trivial. This is because $W(T)$ is a highly temperature dependent function. Characteristically $W(T)$ is a thermally activated function of the form

$$W(T) = s \exp\{-E_A/T\}, \quad (9)$$

where E_A is the activation energy for the remobilization process expressed in temperature units, and the preexponential factor, s , depends upon the coupling constants between the lattice and trapping defect, the trapping cross-section, and the recombination or recapture cross-sections. Fortunately, in most systems these dependencies combine in such a way that " s " is determined almost entirely by the characteristic coupling constant of electrical charge to the lattice structure of the host solid; for ionic solids this value is typically given by the optical

mode lattice vibration frequencies of the material and

$$s \approx 10^{12} \text{ sec}^{-1}. \quad (10)$$

As we shall see, the properties we are interested in depend only logarithmically upon "s" so that as long as "s" is a very large number the approximation given by Eq. 10 is sufficient for our purposes. There are of course peculiar, but well-known, systems in which the approximation of Eq. 10 is not particularly suitable; for example, for the self-trapped case, in which the concentration trapping centers is equal to the number lattice positions in the solid, "s" = 10^8 sec^{-1} , and in cases where the activation energy itself is a temperature dependent quantity due to thermal expansion effects in the lattice, s can appear to be as large as 10^{19} . Because of the logarithmic dependence of properties on s, however, this eleven order of magnitude change results only in factor of 2 change in the temperature scale and may be readily taken into account for any specific system. We therefore continue our discussion on the typical basis of s approximately equal to 10^{12} sec^{-1} .

A complete description of the mathematical behavior has been given elsewhere; it suffices here to say that the ratio of activation energy to peaking temperature, E_A/T_m , depends logarithmically upon s and the temperature scan rate to give a characteristic value

$$(E_A/T_m) \approx 30 = \log_e(10^{14}), \quad (11)$$

and the ratio of half breadth to T_m is given by

$$(\Delta T/T_m) = e(E_A/T_m)^{-1} \approx 0.1. \quad (12)$$

For the factor of 10^{11} change in s which can be observed in some peculiar systems, the value appropriate in Eq. 11 changes only from 22 to 44. Using

the ideas presented above we can now turn to the criteria by which a particular TL phosphor characteristic should be selected for a desired temperature-time thermal dose measurements.

Optimal sensitivity to thermal dose. What is measured in the TL thermal dose method is the fractional fading, $F(T_D, t_d)$, during the thermal dosimetry interval t_d at the effective thermal dose temperature T_D ; we discussed this initially in terms of Eq. 8, and

$$F(T_D, t_d) \equiv L_R L_0^{-1} = \exp\{-W(T_D) t_d\}. \quad (13)$$

Now the criterion for optimal choice of TL phosphors is that one knows the approximate range of values for T_D and that one knows the measuring interval t_d , and one wishes to be most sensitive to variations from the nominally known value T_D . For optimal sensitivity, therefore, one needs only to find the conditions under which the first temperature derivative of F is a maximum value; this may be obtained directly from Eq. 13,

$$d_T F = (d_T W/W)(W t_d \exp\{-W t_d\}), \quad (14)$$

which may be rewritten, using Eq. 9, as

$$d_T F = T_D^{-1} (E_A/T_D) [W t_d \exp\{-W t_d\}]. \quad (15)$$

We note that all of the rapid temperature dependence in Eq. 15 is dominated by the term in square brackets. Therefore the maximum value of $d_T F$ occurs for the maximum value of the term in square brackets in Eq. 15, that is,

$$W(T_D) t_d \approx 1; \text{ for maximum } d_T F. \quad (16)$$

The physical implications of this condition are simple; if $Wt_D \ll 1$, then so little fading has occurred over the dose measuring interval that it would be difficult to detect, whereas, if $Wt_D \gg 1$, there has been a large amount of fading but the remaining signal to measured is becoming undetectably small. While the TL thermal dose technique would be useable for values of Wt_D ranging perhaps from 0.1 to 10, the exponential temperature dependence of W assures that this would not greatly effect the descriptive TL parameters which are chiefly of interest in the present inquiry. For estimating the parameters for optimum sensitivity, therefore, we use Eqs. 9 and 10 and 16 to obtain

$$(E_A/T_D) \approx \log_e(10^{12}t_d). \quad (17)$$

This means that for a given interval t_d monitored at mean thermal dose temperature T_D , the TL phosphor applied must have trapping centers described by an activation energy, E_A , given approximately by the value in Eq. 17. For selection of an appropriate phosphor, one can relate this value to characteristic maximum temperature, T_m , which is determined by reading out a TL phosphor thermogram and is given by Eq. 11; that is, combining Eqs. 11 and 17, we obtain the criteria for optimum sensitivity in thermal dose measurements in the form

$$T_m \approx T_D \{ 1 + 0.03 \log_e(10^{12}t_d) \}. \quad (18)$$

Equation 18 is the primary relation used in selecting phosphors for optimal sensitivity in thermal dose measurements. If one wishes to measure thermal dose described by a temperature-time characteristic having a dose interval t_d and an estimated temperature value of T_D , then the TL phosphor chosen should have a thermogram showing a characteristic peak occurring at the temperature T_m , whose value is given approximately

by the relation in Eq. 18. In Eq. 18 the temperatures are in degrees Kelvin and the time interval is in seconds. We note, for a given dose temperature to be measured, that a variation of measuring time from 30 hours to 1000 days for t_D implies a 25% variation of T_m (as given by Eq. 18) reflecting a 25% variation in the effective activation energy E_A of the TL phosphor employed. Similarly for a given dose interval monitored a variation in T_D from 375°K to 250°K (i.e., the interesting region from -20°C to 100°C) also implies a variation in T_m of about 25% which is achieved by selecting TL phosphors with an appropriate variation in E_A .

It is worthwhile to re-emphasize and review the chief ideas so far described. Typically, one wishes to perform a thermal dose measurement over a known time interval t_D and one knows the approximate thermal dose temperature T_D at which the dosimetry measurement is to be performed. In order to be optimally sensitive to variation in that nominal thermal dose temperature (which is the point of doing the thermal dose measurement) it is necessary that the TL phosphor employed exhibit an activation energy which lies within a very narrow range of values as specified by the temperature-time characteristics of the experiment, T_D and t_D . For simple TL systems an adequate diagnostic for determining this activation energy is to perform a TL thermogram run and note the peaking temperature, T_m , of the TL glow curve. One has found a TL phosphor having the appropriate activation energy when one observes a value of T_m given approximately by the relationship specified in Eq. 18. The main purpose of the present paper is to point out that there are more complex TL systems than those described above; in these systems, it is possible to change the effective activation energies as diagnosed by changes in the observed values of the peaking temperature, T_m . This is accomplished

by changing the initial irradiation and initial thermal annealing procedure. In this way, it is possible to adjust to a range of desired values for the temperature-time characteristics of the TL thermal dose device utilizing only a single TL dosimetry phosphor material.

Complex TL systems. The properties of simple systems described above are characteristic of lightly doped, thermally quenched, single crystal TL phosphor materials. Although such simple systems are by no means rare, the more typical case is one of somewhat greater complexity. An important example for our purposes is calcium sulphate doped with manganese ($\text{CaSO}_4:\text{Mn}$) as a TL activator; this phosphor is commercially available as a fine grained powder suspended in a teflon matrix with 0.5 to 10% loading of the active material. Figure 2 shows the TL thermogram from a $\text{CaSO}_4:\text{Mn}$ phosphor embedded 4% by weight in teflon rods; the radiation exposure for Fig. 2 was approximately 125 rads at room temperature with readout occurring immediately thereafter. The peaking temperature is $T_m = 140^\circ\text{C}$. From the expression for simple TL systems given by Eq. 11, one would expect the breadth at half maximum to be no more than 45°C ; the observed breadth shown in Fig. 2, however, is closer to 70°C . The $\text{CaSO}_4:\text{Mn}$ thermogram shown is actually a broadened distribution of activation energies each component of which would exhibit the narrow thermogram curve as indicated in Fig. 1. While this complexity is undesirable from the point of view of ionizing radiation dosimetry, it is very useful for utilization in thermal dose measurements. This is illustrated in Fig. 3 for which curve I is the $\text{CaSO}_4:\text{Mn}$ -teflon thermogram for a 100 rad exposure followed by immediate readout and curve II is the thermogram for the same sample given a dose of 10^5 rads followed by an annealing treatment at 125°C for 45 minutes and then cooled to room temperature before readout. From Eq. 18, the thermogram characteristic of curve I would be nearly optimal for a 30 day monitoring interval at effective thermal dose temperatures near

the body temperature of mammals, whereas curve II would be an optimal characteristic for thermal dose measurements over a 30 day period near the boiling point of water.

Finer tuning than indicated in Fig. 3 is, of course, also possible; Fig. 4 illustrates (in curve I) the standard thermogram, 125 rads followed immediately by readout, in comparison with a 125 rad dose followed by a one day anneal at 27°C . The resulting shift in T_m is approximately 6°C . An intermediate peaking temperature, not shown in Fig. 4, can be achieved by a 125 rad exposure followed by a 1 minute anneal at 85°C .

These data illustrate the possibilities and indicate the dose-anneal variation methods by which the thermogram temperatures T_m and therefore the desired temperature-time thermal dose measuring characteristic can be varied within a single TL phosphor material. The type ionizing radiation exposure employed also may be utilized in a different way to change the TL thermogram characteristics. This is illustrated in Fig. 5; the solid curve thermogram is characteristic of calcium fluoride uv-grade material exposed to ultraviolet radiation, whereas the dashed line is the TL thermogram resulting from x-ray exposure of the same sample. In both cases the irradiation temperature was 150°K . As can be seen in Fig. 5, different combinations of uv radiations, followed by x-ray irradiation followed by various thermal anneal treatments can produce virtually any desired thermogram shape within a wide range of choice. For example, x-ray exposures followed by annealings to remove all of the peaks below the 340°K peak would yield a thermal dose monitor quite suitable for applications at temperatures near the freezing point of water.

The commercial TLD CaF_2 phosphor, TLD-200, shows a similar composite

of glow peaks occurring from about 110°C to 360°C. This material would be suitable for thermal dose monitoring in the vicinity of room temperature up to ~150°C.

Descriptive theory. The complex TL effects described in the previous section arise from a number of causes. Chief among these are multiple impurity dopings of materials, very heavy impurity dopings leading to impurity aggregation effects, and finely ground powders in which surface state perturbations of the trapping center energies play a large role. The result, one way or the other, is a distribution of activation energies for trapped charges rather than a single unique activation energy. Thus we may consider the trapped charge concentration as comprising a number of subcomponents, n_i , representing the component which decays according to Eq. 1 with rate $W_i(T)$ which characterizes that particular component. Consequently, in place of the simple one component expression given by Eq. 7 we have a complex multi-component decay of the form

$$n(t_R)n_0^{-1} = (\sum_i n_{0i} \exp\{-\int_{t_0}^{t_R} W_i(T) dt\}) (\sum_i n_{0i})^{-1} \quad (19)$$

The combination of different radiation doses, radiation types, and annealing procedures yield different relative distributions of the terms n_{0i} .

In general, these variations result in a shift of the characteristic thermogram peaking temperature. Furthermore, a distribution of activation energies leads to a total light isothermal decay function which is not a simple exponential decay. The thermal fading isothermal decay form is, in fact, a multi-component decay; nevertheless, since a relatively small spread of activation energies is involved, the basic criteria for utilization in a particular time-temperature thermal dose range can

adequately be estimated from the expression in Eq. 18. Exactly what quantitative information about thermal dose is derived from the TL measurement in such complex systems is our next central question of interest.

As we have said previously, the actual isothermal decay dynamics of complex systems is not a simple exponential. These dynamics and their temperature dependence, however, can at the very least be empirically determined for a given set of exposure and anneal conditions. In favorable circumstances, as happens to be the case for the $\text{CaSO}_4:\text{Mn}$ system described earlier, the decay dynamics of the total light output actually may be very accurately described by some simple analytic expression. It is not within the scope of this report to pursue the details; instead, we will discuss the simple case in which the decay dynamics are approximately exponential for the isothermal case, which is a sufficient beginning to indicate how the systems may be quantitatively used in more complex cases and will serve as a beginning point for any subsequent report addressing itself to the finer details. We therefore return to the expression given in Eq. 7.

The total light ratios for a calibration and a readout subsequent to thermal dose exposure gives the fading fraction, $F(t_R)$ as indicated by the notation of Eq. 13. The situation in real thermal dose measurements is when the temperature is not a constant known value; thus, the exponential integral function of Eq. 7 is the appropriate form,

$$F(t_R) = L(t_R)L_0^{-1} = \exp\{-\int_{t_0}^{t_R} W(T) dt\} \quad (20)$$

Insight to the physical meaning of this expression comes from expressing the integral in Eq. 20 as

$$\int_{t_0}^{t_R} W(T) dt = t_d \left[(t_R - t_0)^{-1} \int_{t_0}^{t_R} W(T) dt \right], \quad (21)$$

and realizing that the term in square brackets is, by definition, the time average value of $W(T)$. Consequently, Eq. 21 may be written in the form

$$\int_{t_0}^{t_d} W(T) dt = t_d \int_0^{\infty} P(T) W(T) dT, \quad (22)$$

where $P(T)$ is the statistical probability distribution function that the dosimeter experiences a particular temperature T within the measuring interval t_d . Thus we see that the integral of the decay rate over the dosimetry interval is equal to the product of the dosimetry time and the statistical thermal average value of the decay rate $W(T)$. It is only this thermal average value of the effective decay rate which can be determined from a single measurement of the TL fading fraction. The results may be applied in several ways; for example, if it is known that the temperature load which the dosimeter experiences varies between a single known low value and a single known high value, one can then determine the relative amount of time for which the measured system has experienced the high temperature thermal load. In the complex systems which we have described above, not only can one measure the total light output ratios but one also can determine the shift in peaking temperature, T_m , which occurs between initial preparation of the dosimeter and its subsequent readout after experiencing a thermal dose. With this additional information, one can determine both the thermal average given by Eq. 22 and another quantity, such as the variance in the weighted thermal distribution function, sensed by the dosimeter during the interval t_d .

Summary. Thermal dose monitoring can be accomplished with passive devices by measuring thermoluminescence fading. The chief problem, in a practical sense, is that for measuring in a particular thermal dose interval near temperature T_D , the phosphor must exhibit a TL thermogram

having a particular peaking temperature, T_m . As a rule of thumb, T_m should be approximately 25% larger than T_D in absolute temperature. A number of common TLD phosphors have complex, composite, glow curve thermograms. It is possible, by a combination of initial radiation dose, pre-use annealing, and variation of initial radiation quality, to place T_m at a desired value over a fairly wide range. A particularly attractive material for thermal dose measurements in the 15°C to 100°C range is $\text{CaSO}_4:\text{Mn}$. At lower temperatures, uv-grade CaF_2 seems to be promising, and for higher temperatures, the commercial TLD phosphor $\text{CaF}_2:\text{Dy}$ (TLD-200) has suitable properties.

Fig.1

Fig.3

Fig.2.

Fig.4

Fig. 5