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Present Status of Dosimetry by Radiophotoluminescence and Thermoluminescence Methods

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ABSTRACT

This is a review of the present status of dosimetry by radiophotoluminescence and thermoluminescence devices, including: principles of operation, types of glasses or phosphors available, types of luminescence-measuring instruments, dose-ranges, precision and linearity obtainable, time-stability of dosimeter response, temperature effects during irradiation and storage, dependence upon absorbed dose rate, dependence of response per roentgen upon the effective quantum energy of γ-radiation, response to neutrons, and dependence of response per rad upon linear energy transfer (LET). A brief historical review of each system is presented. Recent developments in infrared stimulable phosphors for dosimetry are also mentioned. A reference list of 97 items is given.

PROBLEM STATUS

This is an interim report on one phase of the problem; work is continuing.

AUTHORIZATION

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PRESENT STATUS OF DOSIMETRY BY RADIOPHOTOLUMINESCENCE AND THERMOLUMINESCENCE METHODS

INTRODUCTION

Many significant advances in radiophotoluminescence and thermoluminescence dosimetry have occurred within the last few years. The present review was undertaken to provide a convenient reference for the increasing numbers of dosimetry investigators who are interested in this field. The reference list of 97 items is by no means exhaustive, but will serve as a useful starting point for those wishing to survey particular subjects in more detail.

RADIOPHOTOLUMINESCENCE IN SILVER-ACTIVATED PHOSPHATE GLASS

Principle of Operation

Schulman et al. (81) found that silver-activated phosphate glass[1] could be used for dosimetry. Ionizing radiation has two effects upon it (see Fig. 1): (a) to increase its optical density over a broad wavelength region in the UV and the visible, and (b) to cause the formation of stable fluorescing centers which continuously emit orange light (5000-7000A) under UV excitation (3650A). The latter stable centers are probably atomic silver, resulting from the capture of a free electron (produced by the γ rays) by a silver ion (Ag^+). The presence of these centers is also partially responsible for the increase in optical density, but other less-stable color centers are also present. Thus the optical density changes in the glass exhibit less stability than do the fluorescence changes, as will be discussed. A bibliography containing many references on phosphate glass dosimetry has been compiled by Raghunath (74).

Types of Glasses and Readers Available

One advantage of this dosimetry system is the present availability of the glass dosimeters in several shapes and glass compositions, and of readers for performing the fluorescence measurements, in the manner shown in Fig. 2.

In its earliest application, the glass was in the form of a block (1.6 × 1.6 × 0.5 cm) contained in a plastic locket to form the Navy's "DT-60" personnel dosimeter (83). Shortly thereafter miniature rods of glass were developed (82) which were small enough (1 mm in diameter by 6 mm long) to allow their use in vivo. The objectionably high atomic number of the original glass,[1] compared with that of tissue or air, led to the development of other

Note: The continued support of the NRL dosimetry program by the Atomic Energy Commission and the National Aeronautics and Space Administration is gratefully acknowledged.

[1] Elemental composition by weight: Ag, 4.3%; Al, 4.7%; K, 7.7%; Ba, 10.8%; P, 28.4%; O, 44.1%.

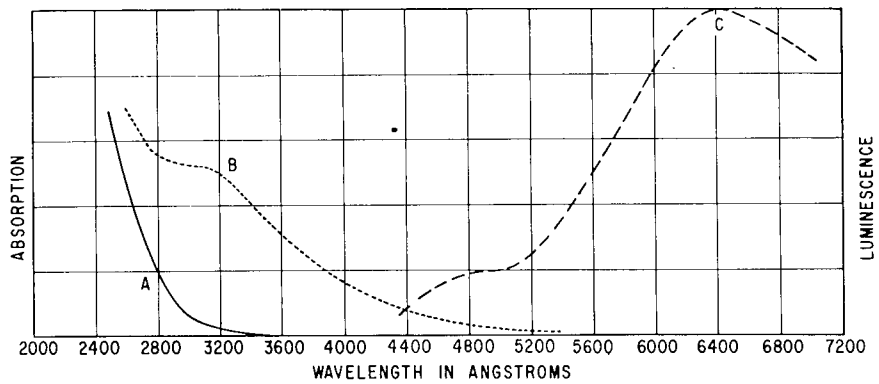

Fig. 1 – Optical spectra for silver-activated phosphate glass[1] (83). (A) Absorption of glass prior to exposure to γ rays; (B) same after a γ-ray exposure, showing growth of absorption in the UV and visible regions; (C) spectrum of (orange) emitted light under 3650A excitation.

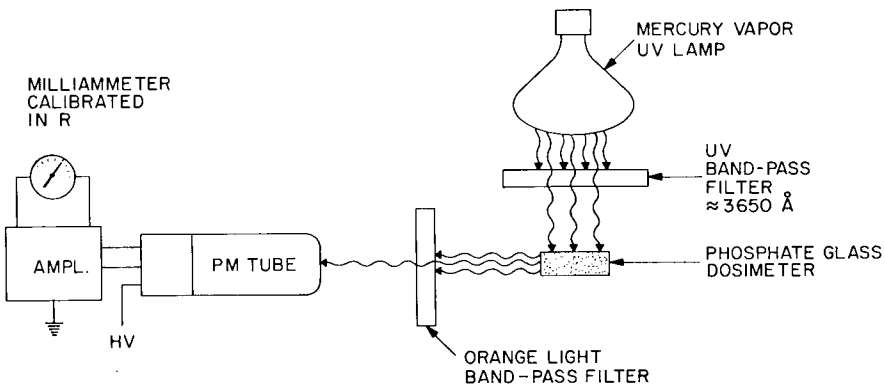

Fig. 2 – Schematic diagram of a fluorimeter for measuring radiophotoluminescence in silver-activated phosphate glass dosimeters

glasses having lower atomic numbers, but generally similar performance characteristics (39)[2] (96).[3] These glasses[1-3] are now all available in the form of miniature rods or various sized blocks or other shapes (e.g. spheres) from at least two manufacturers.[4] Suitable fluorescence readers are available from these companies and at least two others.[5] In fact, any fluorimeter may be used, if suitable optical filters, and some arrangement for holding the glass pieces in a fixed geometry, are provided (13).

[2]Elemental composition by weight: Ag, 4.3%; Al, 4.7%; Li, 1.9%; Mg, 3.1%; P, 33.7%; O, 52.3%.

[3]Elemental composition by weight: Ag, 4.2%; Al, 4.6%; Li, 3.6%; B, 0.8%; P, 33.3%; O, 53.5%. The authors studied other compositions as well, but found this to be the best of the group.

[4]Bausch and Lomb, Inc., Rochester, New York; and, Tokyo Shibaura Electric Co., Ltd., Tokyo.

[5]G. K. Turner Associates, Palo Alto, California; R. A. Stephen and Co., Ltd., Mitcham, England.

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One should not assume that a given type of glass[1-3] will always display the same characteristics regardless of batch. A recent batch of glass rods[1] has been found by the author to have 50% greater γ-ray sensitivity and a slower postexposure buildup of fluorescence than earlier batches of the "same" glass. Variations in the raw materials used in making the glass may be the cause of such marked changes.

Dose Range, Precision and Linearity

The usable dose range of the silver-activated phosphate glass (with fluorescence measurements) has been variously quoted in the literature, as it depends upon the size of the glass piece as well as its orientation with respect to the UV beam in the reader. At large doses the absorption of UV in the glass becomes large enough so that the UV light cannot penetrate through to illuminate the piece completely. Thus the curve of fluorescence brightness vs absorbed dose becomes nonlinear and flattens out, finally decreasing with further increases in dose. The glass appears dark brown in color, indicating that attenuation of the emitted orange light plays a part in decreasing the overall fluorescing efficiency; the UV absorption is the larger effect, however.

The dose at which marked nonlinearity occurs may be as low as 10^3 rad, for an optical path of 13 mm for UV and 6 mm for fluorescent light (71) or it may approach 10^5 rad if neither path length exceeds 1 mm (12,13). Lee et al. (56) report that the usable range can be extended to 10^5 rad for miniature glass rods, regardless of their orientation in the UV beam, by heating them (postexposure) for one hour at 325°C. This treatment was found to bleach out most of the color centers without seriously disturbing the fluorescing centers, as can be seen in Fig. 3.

The minimum detectable dose for DT-60's and for miniature rods of two types[1,2] has generally been found to be about 10 rad. A background fluorescence in the glass, equivalent (in the B&L reader) to the fluorescence produced by 30-40 rad makes smaller readings unreliable.

Recently this limitation has been greatly relaxed through the work of Yokota et al. (96) and Yokota and Nakajima (97). They have developed a glass[3] which (as measured on a B&L reader) has three times the postexposure fluorescence brightness of the high-Z glass rods,[1] with only one-half of the background fluorescence. Further, they designed a fluorimeter (97), which discriminates even more strongly against the background fluorescence, so that it is equivalent to no more than 300 mR for the 1 × 6 mm rods of this glass.[3] Using polished glass blocks 8 mm square × 4.7 mm in thickness, they measured γ-ray exposures of 10 mR with ±15% standard deviation, and 50 mR and higher with ±2% standard deviation. Measurements of this kind, against a relatively large background signal, require the utmost in reader stability and cleanliness of glass samples to avoid shifting of the background level. Washing the dosimeters in acetone, distilled water, and absolute alcohol, in that order, has been widely used.

The precision of readings requires further elaboration. Glass dosimeters have been studied mainly in the form of miniature rods because of their commercial availability along with suitable readers. The problems of manufacturing the rods uniformly, of positioning them positively in the reader, of cleaning them adequately so that fluorescence of surface contamination is not excessive in spite of the large surface-to-volume ratio, and of handling them so that their edges do not become badly chipped are lessened by the use of larger blocks of glass (65,97). It is likely that in future applications not requiring the miniature size, it will purposely be avoided.

It is difficult to summarize briefly the reading-precision data which have been reported for the glass rods, as various readers and techniques have been employed, and the data reported in terms of figures are not readily comparable. However several typical

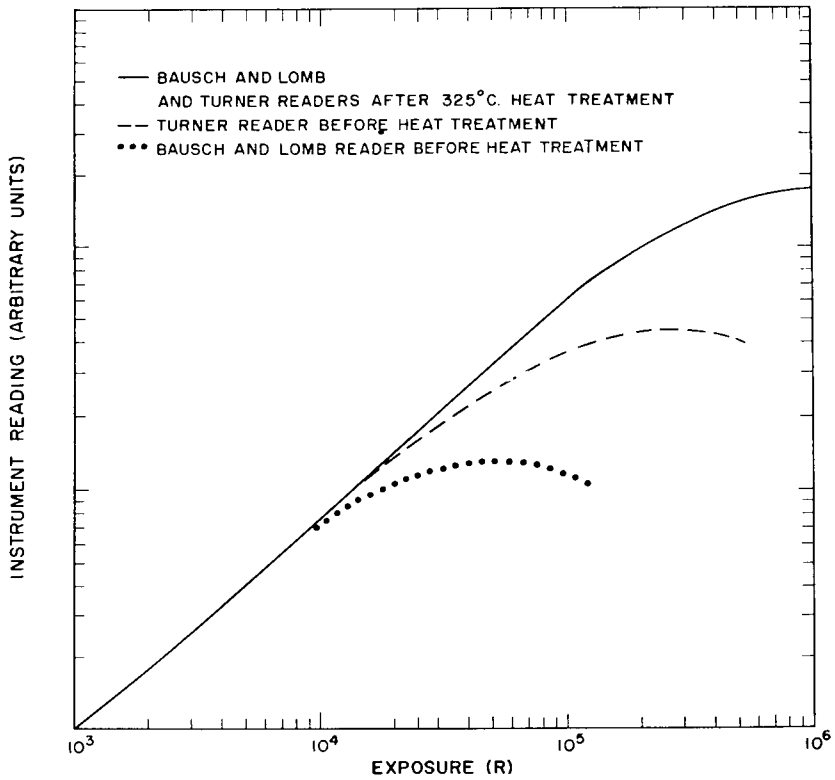

Fig. 3 – Radiophotoluminescence response of silver-activated phosphate glass[1] rods as a function of γ-ray exposure (56). The B&L reader exhibits saturation at a lower exposure because the UV light path in the glass rods is longer than that in the Turner reader. Heat treatment extends the usable range with both readers. Note the sublinearity of the curve even below the onset of optical-density saturation.

examples will convey the order of magnitude of precision which has been observed. Hine et al. (45) reported a standard deviation of ±6% at 1000 rads, in a large group of glass rods measured with the reader described by Barr et al. (12,13). This spread was not decreased by weighing each rod and taking the fluorescence per unit weight. Barr et al. (12) compared two readers (a conventional fluorimeter with a laboratory-constructed glass-rod holder vs the Bausch & Lomb reader) in their ability to measure the fluorescence of rods given various doses from 0 to 2.75×10^5 rads. The standard deviations among ten readings on three rods at each dose ranged from 1 to 8% on both readers, and averaged 3 to 4%, showing no pronounced trend with dose. Standard deviations in the net fluorescence (total minus pre-irradiation fluorescence) would, of course be greater. Barr et al. (13), Oliver (69) and others have observed that the within-batch variations on a given day were smaller than the day-to-day variations of a given glass rod, indicating reader instability. To minimize this, it is advisable to use stable fluorescence standards such as Mn-glass rods in adjusting the reader sensitivity to maintain as nearly stable performance as possible.

In contrast with the foregoing results, Cheka (25) has reported a probable error of only ~2% for measurements with a modified B&L reader, and ~3% for a Turner reader, in measuring γ-ray exposures over 100 R with glass rods of all three types.[1-3] Bramson (20) employing a B&L reader, found "maximum expected errors" ranging from ±30% at 10 R to ±3% at 100 R or more.

One must conclude that the overall within-batch day-to-day precision which can be achieved with care varies considerably from reader to reader and from batch to batch of

glass rods, and might be expected typically to range around 5-10% standard deviation for doses large in comparison with the dose necessary to double the pre-irradiation fluorescence.

The fluorescence (less the background fluorescence) is a strictly linear function of the absorbed dose up to a dose where attenuation of UV becomes important, as previously noted. However, some of the data reported for commercial readers indicate somewhat less-than-linear behavior, as in Fig. 3. (25,56). One should not assume a given reader to be linear, but instead should make a calibration curve of response vs exposure or absorbed dose.

Fluorescence Stability

Recent measurements of Cheka et al. (25) and of Attix and Pfaff (10) are in general agreement that all three types of glass rods[1-3] show some buildup of fluorescence with time after exposure, reaching a maximum after which a steady decrease occurs over a long period of time. Typical behavior at room temperature is shown in Fig. 4 (10). The initial rise is larger in the low-Z glasses than in the high-Z glass; it also takes longer to reach a maximum in the low-Z glasses. Fading appears to be smaller in the low-Z glass, because of the opposing influence of the long-term buildup of fluorescing centers. However after 2 hr heating at 100°C, maximum response is reached and the subsequent fading (3-5% in one month, 15-20% in one year) is roughly the same in the three glasses (Fig. 4). Becker (14) has studied the fluorescence of irradiated glass[3] as a function of time at storage temperatures from 40° to 400°C. At 300°C the fluorescence is practically gone in 100 hr; at 400°C 1 hour accomplishes this. Hodara et al. (46) have heated high-Z glass rods to 400°C for 5 hr, and Cheka (25) has used 450°C for 20 min, to erase the fluorescence and allow reuse of the rods. In all these treatments the pre-exposure fluorescence signal is increased by a few percent.

Effect of Temperature During Irradiation and Reading

Oliver (69) found that the high-Z glass response varied +0.4% per °C as a function of the irradiation temperature, near 25°C. Peirson (71) reported that the temperature of the glass[1] at readout also affected the fluorescence reading, with a coefficient of -0.9% per °C; Schulman et al. (83) reported -0.7% per °C. Thus prolonged retention of a sample in the reader may cause an apparent depression of the reading as the sample warms up.

Rate Dependence

The fluorescence response of all three glasses has been found to be independent of dose rate for x-ray or electron pulses (1 μ sec) at rates at least up to 10^8 rad/sec (89).

Energy Dependence

High-Z glass rods[1] are some 30 times more responsive per roentgen at 70 kev than for Co^{60} γ rays, as indicated in Fig. 5. Low-Z glass,[2,3] shows about 1/3 as much energy dependence. Various shields have been designed to reduce the magnitude of this effect (5,14,29,30,60,65,81,83, and 88). In general, the high-Z glass[1] requires high-Z shields (e.g. gold or platinum), whereas the other glasses are most improved by shields of intermediate Z (e.g. silver or tin). As was first pointed out by Klick (50a), perforations or partial shielding are necessary to preserve response below 100 kev. Directional dependence becomes a problem with the shielded glass rods at low energies, but Becker's design (14) minimizes this.

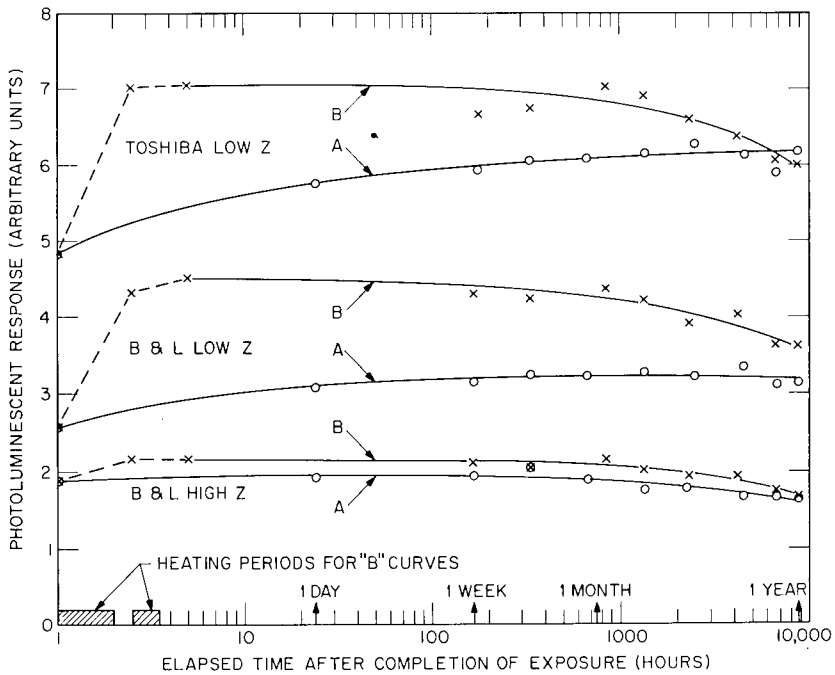

Fig. 4 – Photoluminescence response of silver-activated phosphate glass rods as a function of storage time in the dark at room temperature (10). All rods were given 1000 R of Co^{60} γ-radiation at 280 R/min. Curves B represent rods which were given two 1-hour heat treatments at 100°C, as indicated in the lower left of the figure. Curves A are for rods undergoing identical storage but without the heat treatments.

A different approach involves the use of two or more glass pieces with differing amounts of shielding (5). The ratio of readings gives a measure of the effective energy of γ-rays in an unknown field. This method has been used in personnel-monitoring applications of the glass (42,51, and 65).

In spite of the energy dependence of the glass, several investigators have shown that, at least under narrow beam conditions, the response of even the high-Z glass[1] follows fairly closely the response of air-equivalent ion chambers or ferrous sulfate dosimeters in depth-dose curves (13,46, and 76). The use of low-Z glasses[2,3] and/or metal shields is advisable, however, to minimize the occurrence of erroneous measurements caused by scattered low-energy radiation, particularly under broadbeam conditions.

Response to Neutrons

Thermal Neutrons – The high-Z glass[1] is sensitive to thermal neutrons through the activation and subsequent decay of the silver component. Miniature glass rods are less sensitive than larger pieces because the β rays emitted by the activated silver have long enough ranges to carry 2/3 of their energy out of the rod (52). Even so, they are several times more responsive (per rad in tissue) to thermal neutrons than to Co^{60} γ rays (6). A jacket of lithium can be used to reduce or eliminate the thermal neutron effect (15,32). The lithium-bearing glasses[2,3] are still more sensitive to thermal neutrons; Bernard et al. (15) report 8-fold greater sensitivity in the B&L low-Z glass.[2] The Toshiba glass[3] should be even more so because of a factor-of-two more lithium; the results of Yokota et al. (96) underestimate this because larger glass pieces were used (6).

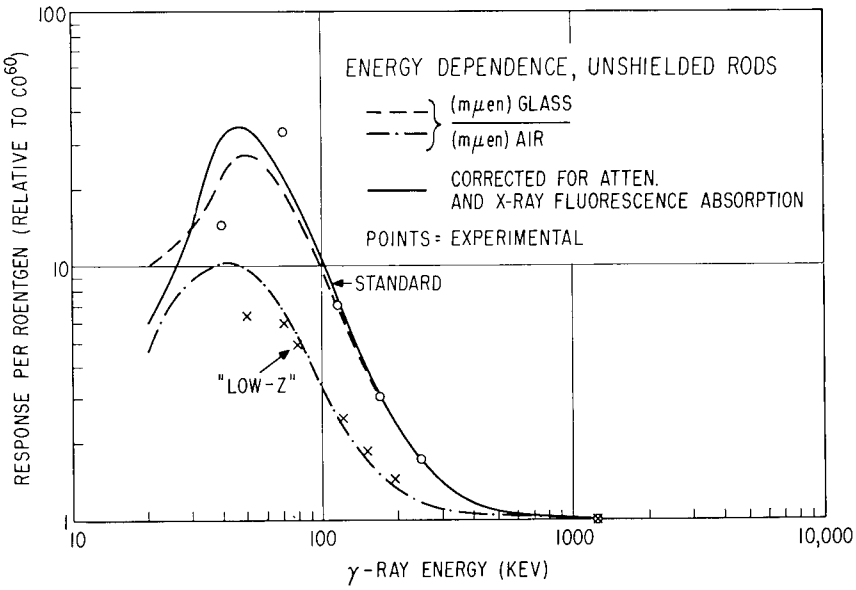

Fig. 5 – Energy dependence of the B&L high-Z and low-Z glass rods[1,2] (7). The Toshiba glass rods[3] have an energy dependence approximating that of the B&L low-Z rods. Dashed curves are calculated ratios of absorbed dose in glass to that in air assuming that the incident γ rays and the characteristic x rays from Ba and Ag in the glass are not attenuated. The solid curve includes corrections for attenuation of primary rays and absorbed dose contributions by the characteristic x rays. The decrease in the glass response per rad at lowest energies is not taken into account.

Fast Neutrons – The fast neutron sensitivity of the high-Z glass[1] is relatively small, being chiefly due to elastic collisions (11,15,52,53,71, and 88). The response per rad (in a small tissue sample) relative to that for Co^{60} γ rays ranges from 0.5 to 0.7% for 0.5 to 1.5 Mev neutrons (15). At 14 Mev the corresponding figure is 3.5% (52). Fast-neutron response of the low-Z glasses is expected to be small also. The response to fast neutrons can be enhanced somewhat by enclosing the rods in hydrogenous envelopes so that recoil protons can enter the glass (52). Nappi and Distenfeld (66) have designed a dosimeter suitable for neutrons from thermal to 18 Mev by enclosing the glass rods in a 20-cm-diameter pressed/wood sphere.

Linear Energy Transfer (LET) Dependence

Kondo (53) found that the response per rad in the high-Z glass[1] depends upon the LET of the radiation, being lower for α-particles and recoil protons than for γ radiation. Tochilin et al. (90) have confirmed this trend in all three glasses[1-3] and found that for sufficiently energetic α-particles (900 Mev) the response of the glass per rad deposited in it is nearly the same as for γ radiation. Ritz and Cheek (77) investigated the response of the high-Z glass[1] to soft x rays, measuring its coloration rather than fluorescence. The response per rad in glass to x rays generated by an unfiltered beryllium window tube operated at 50 kv (constant potential), was only 70% of that for Co^{60} γ rays; at 15 kv the response was down to about 40%. These figures may not apply directly to the fluorescence measurement of the glass, and may differ for the low-Z glasses, but they do indicate that the use of phosphate glass for very low energy x rays or β rays, or other high-LET radiations, should be suspect unless accompanied by an absolute calibration with identical radiation.

THERMOLUMINESCENCE

When a thermoluminescent phosphor is exposed to ionizing radiation while at a sufficiently low temperature, many of the freed electrons (or "holes") become trapped at lattice imperfections in the crystalline solid (Fig. 6). They remain trapped for long periods of time when stored at that temperature (or lower temperatures). If the temperature is raised, the probability of escape is increased and the electrons (or holes) are released from the traps, subsequently recombining with opposite-charge carriers with the emission of light. If the light intensity is measured as indicated schematically in Fig. 7, and plotted as a function of the temperature, or of the time during the period while the temperature is being increased, the resulting graph is called a "glow-curve" (Fig. 8). Typical glow curves exhibit one or more maxima as traps of various energy "depths" are emptied; the relative amplitudes of the peaks indicate approximately the relative populations of trapped electrons in the several trap species, provided the heating rate is constant throughout the glow curve. Faster heating rates result in peaks of greater amplitude with the maxima shifted to higher temperatures.[6] On a graph of light intensity vs temperature, the area under a glow peak is usually increased thereby. On an intensity vs time plot, the peaks become narrower at faster heating rates, and the areas under the peaks (i.e., light sums) are constant unless a peak has been shifted to a high enough temperature to be thermally quenched.[7] The theory of thermoluminescence and the interpretation of glow curves are discussed elsewhere, for example by Randall and Wilkins (75).

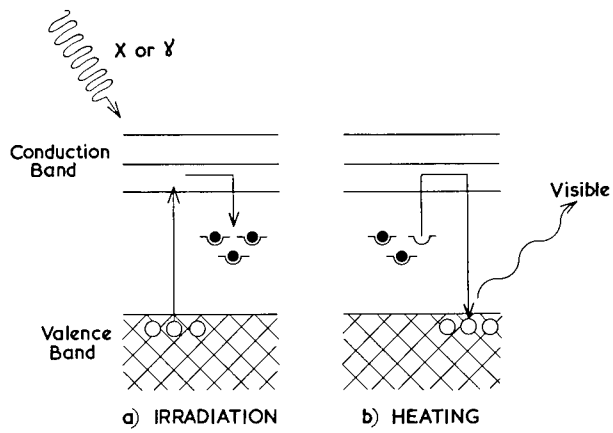

Fig. 6 – Schematic representation of the processes involved in thermoluminescence dosimetry (33). Energy states in the crystal are represented with energy increasing upwards along the ordinate. (a) Irradiation produces free electrons and holes. The electrons are free to travel through the solid in the conduction band, until they are either trapped (black circles), or they fall back into the valence band with the emission of light. (b) On subsequent heating, the trapped electrons are given sufficient thermal energy to escape from the traps, and upon return to the valence band (and recombination with a hole), they emit light. The total quantity of light emitted during heating process is proportional to the number of electrons released from traps, unless the temperature becomes high enough for "thermal quenching" to take place, in which case electrons may return to the valence band without emitting light.

[6] Note that the apparent temperature at which a glow peak occurs is quite variable, influenced not only by an inherent dependence of the glow peak temperature upon the heating rate, (see (75)), but also by the closeness of the thermal contact between the thermocouple and the phosphor, and by thermal radiation losses from the phosphor (24). In a typical dosimetry-readout system where fast heating rates are used to improve the signal-to-noise ratio, all of the foregoing effects operate to increase the apparent temperature of a glow peak maximum.

[7] The author is indebted to Dr. J. H. Schulman, who first suggested the existence of this latter effect.

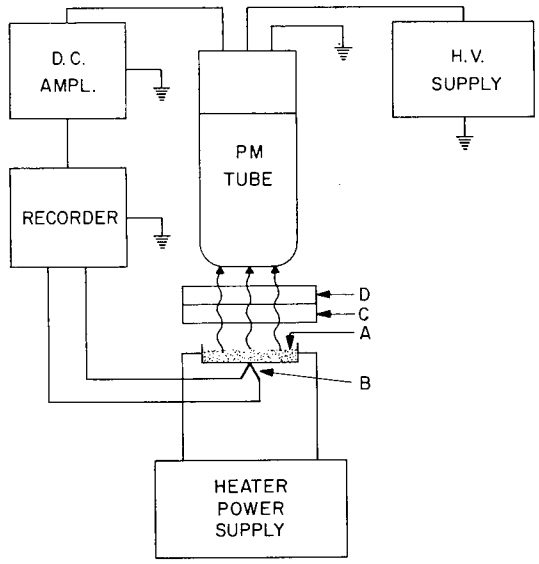

Fig. 7 – Schematic diagram of a thermoluminescent-dosimeter reader. (A) Heater pan containing either loose powdered thermoluminescent phosphor, or a sealed dosimeter; (B) thermocouple in contact with the pan; (C) an infrared-light-rejecting optical filter; (D) a band-pass filter suitable for the thermoluminescent light. The recorder may be either: (a) a current vs time chart recorder; (b) a current-vs-temperature chart recorder; (c) a peak-height-recording microammeter; or, (d) a charge-integrating circuit. Display of the glow curve (i.e., use of (a) or (b)) is preferable for studying thermoluminescent dosimeters, and is often used in conjunction with (d).

Either the light sum during part or all of the glow curve, or the height of one or more of the peaks, may serve as a measure of the absorbed dose in the phosphor or the γ-ray exposure it has received. In case the peak height is used for this, the heating cycle must be sufficiently reproducible to avoid causing peak-height fluctuations. Heating-rate uniformity throughout the glow curve is, however, generally not required. After the traps have been emptied by heating at a high enough temperature for a sufficient length of time, and the phosphor subsequently cooled, it is normally returned to its original condition and is ready to register another exposure to radiation.

There are a large number of thermoluminescent materials; in fact most solid materials thermoluminesce to some degree. It is interesting that the thermoluminescence of roof tiles in Hiroshima has been measured in an attempt to verify estimates of dose (in hundreds of rad) from the atomic bomb explosion 17 years earlier (44). Thermoluminescence has also been employed in dating meteorites (41), and minerals and ancient pottery (27). A bibliography on thermoluminescence has been compiled by Angino and Grögler (2).

To be useful for normal dosimetry applications a thermoluminescent phosphor must at least have a relatively strong light output and the ability to trap and retain electrons for reasonable periods of time while at room temperatures, or at the temperatures to be encountered in application. This effectively limits the useful phosphors to those having traps at about 80°C or above, so that thermal release of the trapped electrons at room temperature is at least not too rapid to be accounted for by a correction factor. Three such phosphors, which have been extensively reported upon in the literature, will be reviewed here. They are outstanding in being able to measure doses down to the millirad (or even microrad) region, and for having very wide linear ranges of response vs dose.

Calcium Sulfate

Manganese-activated calcium sulfate ($CaSO_4$:Mn) has a long history as a thermoluminescent detector of ionizing radiation (58,95). Tousey et al. (91) used it to measure solar UV and x rays in rocket flights. Kossel et al. (54) employed it as a means of measuring dose in body cavities.

The method of phosphor preparation described by Watanabe (93) has been widely employed by later investigators, with some variations in detail. This phosphor has a glow

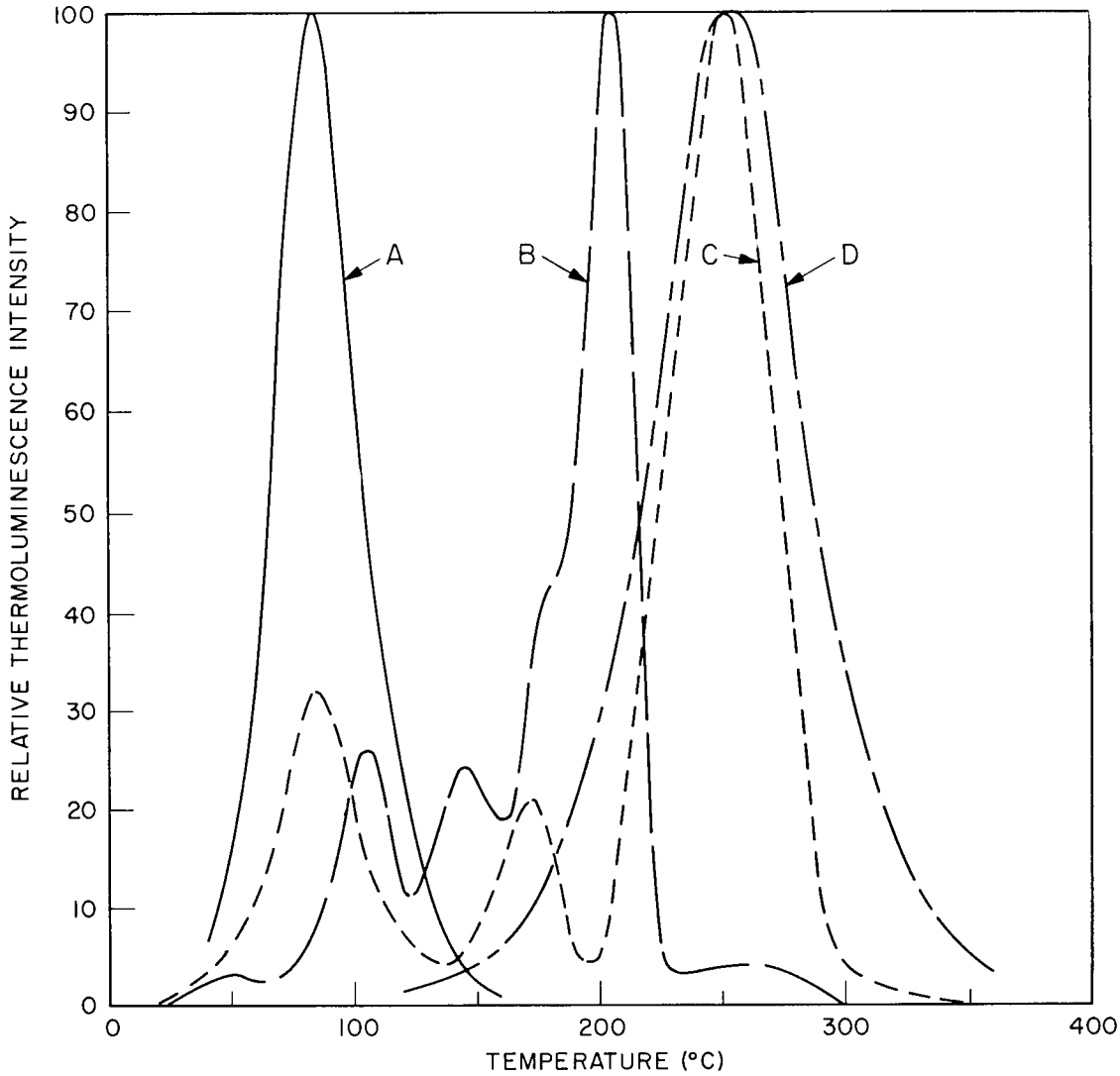

Fig. 8 – Typical thermoluminescence glow curves, intensity vs temperature. The maximum intensity of each curve is arbitrarily set at a value of 100. (A) $CaSO_4$: Mn (70); heating rate 6°C/min. (B) LiF (TLD-100) ((86); also Ginther, private communication); 10^4 R exposure, heating rate 20° C/min. Note that the peaks at 100° and 150°C can be suppressed by preirradiation annealing procedures (23). (C) CaF_2 (M.B.L.E.) (80); about 20 rad from β rays, heating rate 60°C/min. (D) CaF_2:Mn (NRL) ((85); also Ginther, private communication); 10^4 R exposure, heating rate 20° C/min.

curve as shown in Fig. 8, with a single maximum occurring at 80-100°C. Arkhangel'skaya et al. (4) and Bjärngard (17) have measured the light spectrum; they report that it extends from about 4500A to 5900A, with the maximum near 5000A (see Fig. 9).

The rates of fading of light sum after exposure which have been reported by various investigators differ considerably. The following table summarizes the losses observed after storage times of 10 hours, 3 days, and 8 days at room temperature. Minor differences in phosphor preparation and storage temperatures probably account for the variability. The necessity for measuring and correcting for the fading losses in dosimetry applications is clearly indicated, and is the main disadvantage of $CaSO_4$:Mn.

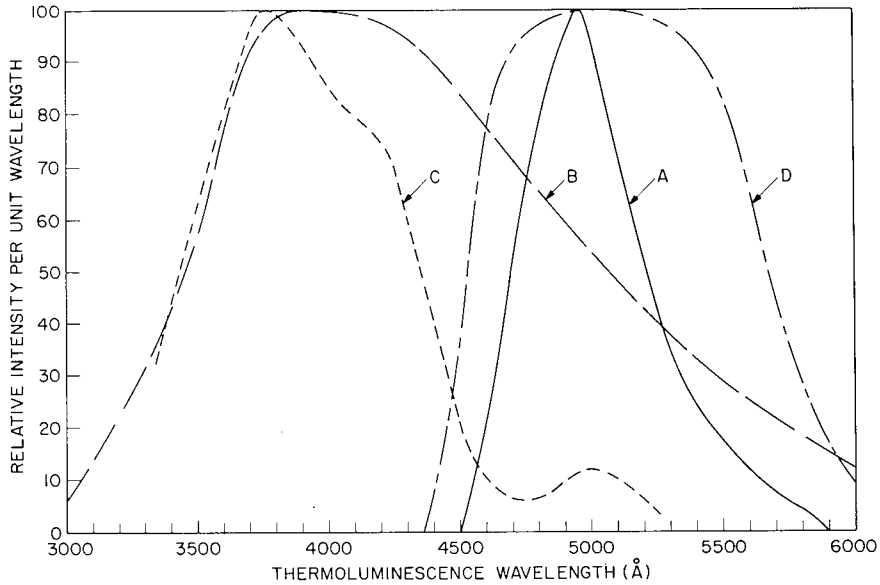

Fig. 9 – Thermoluminescence emission spectra, normalized to a peak emission intensity per unit wavelength of 100. (A) $CaSO_4$:Mn (17). (B) LiF (TLD-100) (Cameron, private communication, 1964). (C) CaF_2 (M.B.L.E.) (80) and private communication. (D) CaF_2: Mn (NRL) (19), also private communication. Each spectrum is that of the light emitted during the principal glow peak of the glow curves given in Fig. 8. Differences in spectra for other glow peaks have been noted with CaF_2 (M.B.L.E.) (80) and with LiF (TLD-100) (48).

Investigator	Reference	Loss (%)		
		10 Hr	3 Days	8 Days
Patterson and Friedman	(70)	40	70	85
Arkhangel'skaya et al.	(4)	15	43	55
Spurný	(87)	60	85	-
Bjärngard	(17)	27	-	-

This disadvantage is balanced by an outstanding advantage: the ability of the phosphor to measure exposures down to the microroentgen range. This is not due primarily to an inherently higher efficiency.[8] Rather, the fact that the glow peak is located at a relatively

[8] Bjärngard (17) has pointed out that only 1.5% of the absorbed dose in $CaSO_4$:Mn is later re-emitted in the form of thermoluminescent light energy. This may be compared to a corresponding figure of 2.4% for a modified natural CaF_2:Mn supplied to Bjärngard by MBLE Ltd., Brussels. Such data are not yet available for synthetic CaF_2:Mn (37) or for Harshaw TLD-100 LiF. However, Ginther (private communication) finds that $CaSO_4$:Mn and synthetic CaF_2:Mn are about equally sensitive to γ rays, while LiF (TLD-100) is 3 to 7 times less, depending upon the PM tube and filters used.

low temperature results in a relatively small incandescent background signal emitted by the heater and the hot phosphor itself. This thermal background signal is the ultimate limitation on low dose measurements with phosphors (e.g., CaF_2:Mn and LiF) having glow peaks occurring at considerably higher temperatures, even with optimum use of heat-rejecting filters.

The ability of $CaSO_4$:Mn to detect small exposures has recently been exploited fully by Bjärngard (16-18), who has measured 20 μR of Co^{60} γ rays with a standard deviation of ±50%. Prior to his work, the lowest detectable exposures reported for this phosphor were in the neighborhood of 1 to 10 mR (4,68,70, and 87). Bjärngard (18) used large phosphor samples (0.44g) cemented onto Kanthal heater strips with Dow Corning 805 silicone resin. The photomultiplier tube (EMI 6097S) was cooled to 0°C and run at only 630 v to minimize dark current. An interference filter at 5080A and an infrared-absorbing filter were both employed to diminish further the small heat signal. It was found necessary to subtract the thermoluminescence measured with "control" dosimeters of the same type, having received identical handling since the pre-exposure annealing (250°C for 30 min). Typically, after a two-hour period between preannealing and readout, dosimeters exposed to 20 μR gave a reading of 1.3×10^{-10} as compared with control readings of 1.0×10^{-10} (in coulombs of charge from the PM tube anode during 54 seconds of heating time). Still further improvements in usable sensitivity may be possible with $CaSO_4$:Mn, e.g. by cooling the PM tube to a lower temperature to reduce the dark current still more.

The curve of response vs γ-ray exposure for $CaSO_4$:Mn is found to be linear by all investigators, but they disagree about the upper limit at which some form of saturation commences. Spurný (87) found this limit at about 10^4 R, Bjärngard at 5×10^3 R; Felszerfalvi and Patko (31) found no saturation at least to 1500 R, while Arkhangel'skaya et al. (4) observed nonlinear behavior above 400 R. Here again, as in the case of fading during storage, variability in phosphor preparation is probably involved. Bjärngard (17,18) reports that excitation of the phosphor by light and by mechanical disturbances gives signals no greater than that of a 1-mR γ-ray exposure. With care these can be practically eliminated.

Peter (72) and Krasnaya et al. (55) have investigated the performance of a calcium sulfate phosphor with a different activator, samarium. The latter authors described their phosphor as having a glow curve with three maxima, at 65, 120, and 200°C; the 200°C peak was found to contain 90% of the total light sum, and to exhibit negligible fading in 1 month. Linear response vs γ-ray exposure extended from 0.1 to 25,000 R, and light output per roentgen per gram was about 2.5 times that from $CaSO_4$:Mn. However, the emitted light was observed to lie in the wavelength range 5900-6200A. Visible light caused marked fading of the stored signal. Peter (72) described a glow curve having an additional (and predominating) peak at 300°C. He found that the glow curve was drastically changed by operating the phosphor in argon instead of air. Nevertheless, in air, he found a linear peak height response vs exposure extending from 0.005 to 3000 R. $CaSO_4$:Sm seems at present to offer no clear advantage over the other phosphors reviewed here, although it probably deserves further investigation in view of the fading stability observed by Krasnaya et al. (55).

Calcium Fluoride

Natural Calcium Fluoride – CaF_2 occurs in nature as the mineral "fluorite," which usually exhibits a strong radiation-induced thermoluminescence (although its characteristics are variable from sample to sample). Radiothermoluminescence of fluorite was probably studied first by Wiedemann in 1903, and later reported upon extensively by Przibram (1924-1936), Wick and co-workers (1925-1931), Iwase (1933-1934), Hill and Aron (1953), Bohun (1955), Görlick et al. (40), and others; see bibliography by Angino and Grögler (2) and Ginther and Kirk (37). Luchner (57) and Grögler, Houtermans, and

Stauffer (41) studied Wölsendorf fluorite from the point of view of its applicability for dosimetry. Both studies reported three principal peaks in the glow curve with maxima at about 70-100°C, 150-190°C, and 250-300°C, and that only the lowest temperature peak exhibited serious fading with storage time. Schayes et al. (80) have recently employed an unspecified type of CaF_2, whose glow curve (see Fig. 8) nearly resembles that of Wölsendorf fluorite (except for a more pronounced peak at 250°C), in devising thermoluminescent dosimeters enclosed in evacuated glass envelopes similar to those used by Schulman et al. (85). The height of the 250°C peak was reported to be very stable with storage time at room temperature. The wavelength maximum of this thermoluminescence glow peak is at 3800A (Fig. 9) allowing very efficient filtering discrimination against thermal emission by the heater, in spite of the high glow-peak temperature.[9] The usable linear range of peak-height vs γ-ray exposure extends from a few mR to 5000 R, with ±2% standard deviation reported (although probably not extended down to the lower range limit).

A peculiar kind of light sensitivity was observed. When the phosphor was exposed to 4000A light for several hours, a fading of the 250°C peak was observed if a prior γ-ray exposure of about 40 R or more had been given. If the prior exposure was less than 40 R, a buildup of the same peak was noted, indicating additional filling of traps.

Neutron sensitivity was reported to be negligible for fast neutrons, and about the same for thermal neutrons as for γ rays, per rem in tissue. A lead filter is provided in the pencil-shaped dosimeter case to make the γ-ray response per roentgen constant within ±20-30% from 80 kev to 1.2 Mev. These dosimeters and suitable readers are commercially available from MBLE, Brussels.[10]

Synthetic Calcium Fluoride – Wick and Slattery (94) performed an early investigation of the effect of x rays on a synthetic calcium fluoride. Ginther (36) and later Ginther and Kirk (37,38) studied methods for the preparation of a CaF_2:Mn which had only one apparent glow peak, located at high enough temperature for storage stability. Three mole-percent manganese concentration in CaF_2 was found to be optimum, and they investigated the dosimetry applicability of this phosphor employed as a loose powder (37). The glow peak maximum occurs at about 260°C (Fig. 8) and its thermoluminescence spectrum extends from 4500A to about 6000A, with the maximum at 5000A (Fig. 9).

A spurious thermoluminescence, equivalent in glow peak height to that from about 1 R of Co^{60} γ rays, was observed by Ginther and Kirk (37) and ascribed to tribothermoluminescence (i.e. friction amongst phosphor crystals). Schulman et al. (84) attempted its elimination through rigidly mounting the phosphor in a glassy matrix, and were partially successful, lowering the spurious signal to some 50 mR equivalent. Meanwhile, Häring and Schön (43), using a similar type of CaF_2:Mn but prepared by a different technique, made dosimeters consisting of metal strips with the phosphor fastened on with silicone cement. They also were troubled by spurious signals, as large as 100 mR equivalent. They tried coating the phosphor with a conducting SnO layer, which suppressed the spurious signal but also resulted in a fading of 10% per week in the radiation-induced glow peak.

Schulman et al. (85) discovered that the presence of air, rather than tribothermoluminescence, was the primary cause of the spurious thermoluminescence. Enclosing the phosphor in a vacuum or inert gas eliminated the difficulty. Using about 100 mg of phosphor cemented to a graphite heater in an evacuated bulb, the glow peak height was found to be linearly related to the Co^{60} γ-ray exposure from 2 mR to 2×10^5 R, with a reproducibility of about ±2% standard deviation except at the low end of the range. Independence of

[9]Note that $CaSO_4$:Mn and CaF_2:Mn (synthetic) have their maximum emitted wavelengths at 5000A and LiF (TLD-100) at about 4000A.

[10]Manufacture Belge de Lampes et de Material Electronique S. A. (see (80)).

exposure rate was verified at least to 120 R/sec, and this probably extends to much higher rates. An initial fading of the glow peak height of 10% in 16 hours, followed by 1% or less per day at room temperature was noted. However, Ginther (private communication) found that this was absent when slow, constant heating rates were used during readout. The response per roentgen was about 13-fold greater at 40 kev than for Co^{60} γ rays (Fig. 10), but a tin filter was designed to produce an essentially flat response over this range of energies. The work of Schulman et al. (85) formed the basis for a personnel dosimetry system designed at E. G. & G., Inc.[11] by Blase et al. (19) under U. S. Navy Contract. CaF_2 dosimeters and readers are available commercially.[10,11] Miniature thermoluminescent dosimeters, 1 mm in diameter by 12 mm in length, have been developed for use in vivo or for other limited-volume applications (7,8,9,59,61, and 86). These dosimeters have characteristics similar to the larger CaF_2:Mn dosimeter (85) but contain about 8 mg of phosphor, and are useful only down to about 10 mR. Figure 11 shows the glow-peak-height response vs γ-ray exposure for such dosimeters containing CaF_2:Mn (or LiF), from 10^{-1} to 10^6 R.

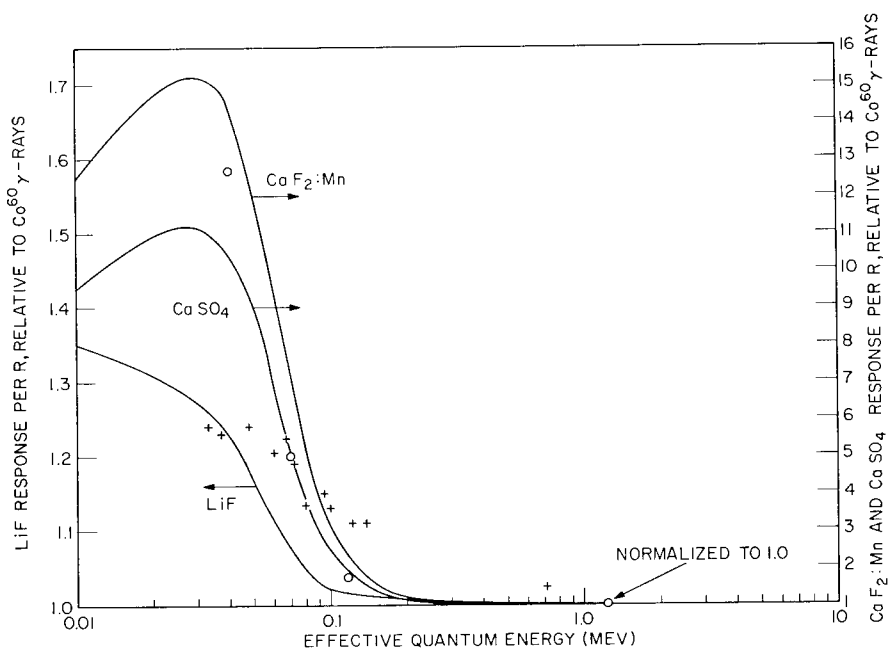

Fig. 10 – Dependence of thermoluminescence response per roentgen upon γ-ray quantum energy. All data are normalized to 1.00 at 1.25 Mev (Co^{60} γ-rays). Curves are calculated on the basis of $(\tau + \mu_{en})/(\mu_{en})_{air}$, in cm^2/g, under the assumption of constant response per rad in the phosphor. Circled points were measured with miniature CaF_2: Mn dosimeters irradiated by heavily filtered x rays (9). Crosses represent the data of Cameron et al. (23), comparing bare LiF (TLD-100) powder with an NBS-calibrated Victoreen 25-R chamber.

[11] Edgerton, Germeshausen, and Grier, Inc., Santa Barbara, Calif.; Metcom, Inc., Salem, Mass.

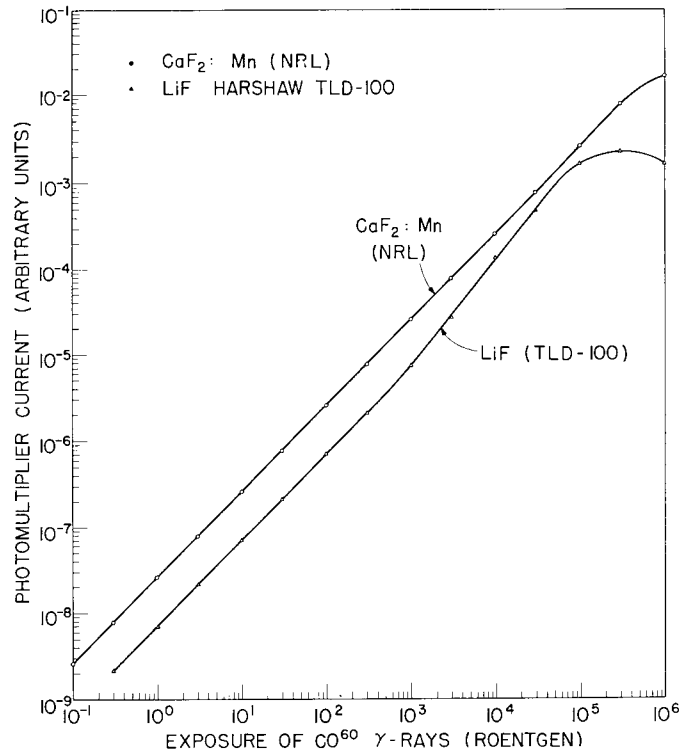

Fig. 11 – Thermoluminescent response (glow peak maximum) of CaF_2:Mn and LiF miniature dosimeters vs Co^{60} γ-ray exposure (62). Previously unexposed LiF dosimeters were used for each point above 100 R.

The thermal neutron response of these dosimeters was found to be such that about 4×10^9 neutrons/cm^2 produced a thermoluminescence equal to that from 1 R of Co^{60} γ rays. Häring and Schön (43) reported that CaF_2:Mn was completely insensitive to neutrons, but by coating the phosphor with Li^6 they were able to detect 5×10^3 thermal neutrons/cm^2. Providing a thick hydrogenous moderator around the dosimeter would allow initially fast neutrons to be detected. Alternatively, the close coupling of hydrogenous material with the phosphor grains may give rise to some fast-neutron sensitivity through energy deposited in the phosphor by recoil protons. This will probably be a weak effect, however, as the phosphor is relatively insensitive to high-LET particles (90).

Frank and Herforth (34) synthesized a CaF_2:Mn phosphor with 6.5 mole-percent Mn activation and a single glow maximum at 210°C. It showed light-sum fading similar in magnitude to the peak-height fading reported by Schulman et al. (85). The usable linear range of light-sum vs exposure extended at least from 1 to 10^4 rad. Adler (1) and Görlick et al. (40) have studied the thermoluminescence of CaF_2 with a number of different activators. A large variety of glow-curve-shapes and emission spectra were found, but none of these phosphors appears to be outstanding for dosimetry applications.

Lithium Fluoride

Daniels and his co-workers (26,27,28) pioneered in the attempt to apply LiF in dosimetry. They made pressed pellets of powdered Harshaw LiF for ease of handling. Fading of an unstable glow peak at 120°C was found to be troublesome in the light-sum reading

technique which they employed, and attempts to eliminate this peak were not successful. Another difficulty is best described by a quotation from Daniels and Rieman (28):

"The question arises as to whether these dosimeters can be used over and over again Each exposure and heating,[12] however, increases the sensitivity sometimes by a factor of two or more. After an exposure of 50,000 roentgens or so, a saturation point is reached beyond which further radiation does not affect the sensitivity. Attempts were made to sensitize pellets by long pre-irradiation, but the results were unsatisfactory. For low exposures, the readings are erratic."

Daniels and Rieman finally decided to abandon LiF in favor of fused aluminum oxide, which they reported to be more stable in sensitivity (which was about half that of LiF), and free from glow peaks below 170°C.[13]

Several years later at the same laboratory Cameron, Daniels, Johnson, and Kenney (22) revived the investigation of LiF, using the identical supply of Harshaw crystal fragments employed earlier by Daniels et al. This time the phosphor was employed as a loose powder without pelletizing, was annealed for a few minutes at 100°C after each exposure to "erase" the low-temperature glow peaks, and was annealed at 400°C for 1 hour prior to reuse to return the phosphor to its original sensitivity (Cameron, private communication). Cameron found that newly procured supplies of Harshaw LiF crystals did not possess an adequately large thermoluminescence glow peak at 210°C, as had been present in the earlier material and had been responsible for its applicability as a dosimeter. In cooperation with Cameron, the Harshaw Chemical Company developed a thermoluminescent-grade LiF called "TLD-100," which is now commercially available.[14] This phosphor exhibits a glow curve as shown in Fig. 8, and a thermoluminescence spectrum as in Fig. 9, having its maximum at about 4000A.

LiF (TLD-100) has received great attention as a dosimetry phosphor because of several particularly advantageous characteristics:

1. Nearly flat response per roentgen over a wide range of γ-ray energies (Fig. 10). At 30 kev it is only 25% greater than at 1.2 Mev, and this remaining 25% can be practically eliminated by suitable shielding (23).

2. A usable γ-ray sensitivity within a factor of two or three of that exhibited by CaF_2:Mn (synthetic). The emitted light from LiF is bluer ($\approx$4000A) than that from CaF_2:Mn ($\approx$5000A), making it possible to discriminate more strongly against the thermal radiation by means of filters. The 210°C glow peak (vs 260°C for CaF_2:Mn) is also favorable in this respect.

3. The light-sum in the 210°C glow peak exhibits practically no fading with storage time at room temperature. Cameron et al. (23) report fading of less than 5% per year.

In addition, this phosphor has a wide usable range of response vs γ-ray exposure, as shown in Fig. 11, which refers to the 210°C glow-peak height (62). The curve is linear up

[12] It is not clear from the reference exactly what temperature or duration of heating was used.

[13] Kenney and Cameron (49) have described the use of pairs of LiF and Al_2O_3 dosimeters in determining the effective energy of an unknown field of x rays.

[14] The activator(s) responsible for the 210°C glow peak in LiF-TLD-100 have not been published, but magnesium is probably the major one, possibly in conjunction with another co-activator.

to about 700 R, then the response becomes proportional to $(R)^{1.2}$ up to about 3×10^4 R, above which saturation begins. This enhancement of phosphor sensitivity by the radiation itself can be annealed out by a heat treatment of 15 min at 400°C (62), which returns the phosphor to its original sensitivity. Cameron et al. (23) recommend instead an annealing procedure of 1-1/2 hr at 400°C followed by 24 hours at 80°C, which is reported to reduce the relative size of the unstable low temperature peaks, making negligible their contribution to the light-sum. If the peak height is used instead of the light-sum as the measured parameter, this special annealing is not needed.

The upper limit of the usable range of LiF (TLD-100) is set by the saturation, which becomes pronounced at 10^5 R (see Fig. 11). This curve-saturation is evidently an indication of another mode of damage in the LiF crystals, which cannot be annealed out at 400°C, (62). Figure 12 illustrates the magnitude of this effect, which is amplified by alternating the γ-ray exposures with annealing periods at 400°C.

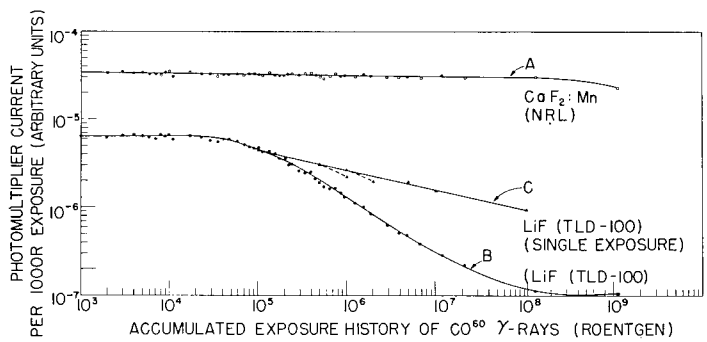

Fig. 12 – Illustration of γ-ray damage in CaF_2:Mn (NRL) and LiF (TLD-100) (62). Points represent glow-peak-height response to 1000 R "test" exposures of Co^{60} γ rays, and are plotted as a function of the total prior exposure received by the dosimeters since manufacture. Each exposure is preceded by an annealing period of 15 min at 400°C. Curve (A) indicates that the response of CaF_2:Mn to the test exposure decreases by about two percent per decade of total exposure history from 10^3 to 10^8 R, above which a sharper decline is observed. Curve (B) shows the corresponding data for LiF (TLD-100), indicating the onset of damage above 3×10^4 R. Curve (C) was obtained by large single exposures of new dosimeters followed by 400°C annealing and then the 1000-R test exposure. Damage is more severe in (B) than in (C) because of a damage-enhancing effect of alternating exposure periods with heating periods (62).

The lower limit of the usable range of exposures is set by the presence of spurious effects caused either by ambient air, or by tribothermoluminescence, or both. Cameron et al. (23) report this spurious signal to be of the order of 1 R equivalent when the LiF is used as a loose powder. Karzmakr et al. (48) have found that the spurious signal behaves as if it were a tribothermoluminescence glow peak occurring some 100°C higher in temperature than the main radiation-induced glow peak in LiF, and having a somewhat longer wavelength. A Wratten 47B filter discriminated against the spurious peak by a factor of two. Nevertheless, the "toe" of the spurious peak interfered with the measurement of the light sum of the radiation-induced glow-peak for exposures below 1 R, and

placed the lower limit of usable range at 0.3 R. McCall and Fix (64) found that filling the reader enclosure with dry nitrogen diminished the spurious signals to the extent that 10 mR could be detected, suggesting that gas effects might be present, being influential only during the readout heating process. Nash et al. (67) have verified this, and have shown that N_2 behaves as a specific "quencher" for spurious thermoluminescence in LiF, while argon is more effective with several other phosphors.

Permanent encapsulation of the LiF powder in glass (9), allows its use down to 10 mR by minimizing gas effects and tribothermoluminescence. Phillips et al. (73) have designed a dosimeter in which the LiF is cemented to graphite cloth with potassium silicate and enclosed between two layers of mica. They report that 20 mR is detectable with this arrangement. Frank (35) cemented LiF powder between aluminum and glass sheets by means of epoxy cement, but found that a spurious signal interfered with measurements below 1 R. Frank's LiF was unlike TLD-100; the main glow peak occurred at 100°C.

The dose-rate dependence of LiF (TLD-100) has been found by Karzmark et al. (48) to be negligible at least up to 2×10^8 rad/sec, using 15-Mev-electron-beam pulses of 1.3 μsec duration.

For measuring neutron fields, two other LiF phosphors are available in addition to the usual TLD-100, which is made from lithium having the natural isotopic ratio (92.6% Li^7 + 7.4% Li^6). TLD-700 is made from 99.993% pure Li^7 isotope, while TLD-600 is highly enriched in Li^6. The thermal neutron cross section of Li^7 is negligible in comparison with the 945-barn cross section for the (n, α) reaction in Li^6. Thus TLD-700 has a negligible response to thermal neutrons compared with TLD-100 or TLD-600. Either of the latter two can be used as a pair with a dosimeter of TLD-700 to differentiate between γ rays and thermal neutrons in a mixed field. Cameron et al. (23) report that TLD-700 has less than 0.5% of the thermal neutron response of TLD-100, hence the TLD-700 measures essentially the γ rays only. The amount of light from TLD-100 which has been exposed to about 2.7×10^7 n/cm^2 (thermal) equals that from a γ-ray exposure of 1 R; 10^8 fast neutrons per cm^2 cause less response in either TLD-100 or TLD-700 than does 1 R of γ radiation (23). The fast-neutron response is so low that it is very difficult to determine with available fast-neutron fields, containing several percent of γ-ray contamination. Karzmark et al. (48) reported that immersing these phosphors in alcohol produced some enhancement of fast neutron sensitivity, but that the response of these phosphors per rad to the resulting recoil protons was only about one-tenth of the response per rad to high-energy x rays. This large LET-dependence of LiF (TLD-100) was also observed by Tochilin et al. (90) for α particles and protons.

The preceding discussions apply primarily to LiF (TLD-100 and where appropriate to TLD-600 or TLD-700) as supplied by Harshaw. Another supplier of dosimetry-grade LiF is Controls for Radiation, Inc. (Cambridge, Massachusetts); their phosphor will not necessarily be identical in behavior to TLD-100. In fact, one should never assume that different batches of LiF, even from the same manufacturer, will exhibit the same γ-ray response. The best procedure is to obtain a large single well-mixed batch, and to run a calibration curve for it over the γ-ray exposure range of interest, using a known γ-ray field. When the total prior exposure of a given sample of TLD-100 phosphor approaches 10^5 R, it should be retired from service, as its γ-ray response will be significantly diminished (62). This dictates against mixing phosphor samples having varying total exposure histories. Using samples once and then discarding them offers a convenient (but, at present, expensive) solution. Several laboratories are investigating the problem of making LiF with optimized dosimetry properties. As mentioned previously,[14] the activator(s) in TLD-100 giving rise to the 210°C glow peak have not been published. Bräunlich and Scharmann (21) and Frank (35) have studied the dosimetry characteristics of other types of LiF. Bräunlich and Scharmann made their own phosphor, without intentional doping (addition of activators); they nevertheless found a strong glow peak near 200°C. Frank used commercially available pure LiF which he subjected to OH^- ion doping and several other processing steps.

The resulting phosphor had its major glow peak at 100°C, and exhibited fading during room-temperature storage. It is evident that LiF is capable of exhibiting a large variety of thermoluminescence behavior, depending upon its preparation.

LiF dosimeters are already in use for clinical dosimetry (23,61), radiobiological dosimetry (48), and even space dosimetry (92). Kenney et al. (50) have described a convenient and inexpensive reader; suitable readers for the loose LiF powder are also manufactured commercially[15] (63). LiF offers a very promising dosimetry system, particularly where flat energy-dependence is of primary importance.

OPTICALLY STIMULATED LUMINESCENCE

Some thermoluminescent phosphors can be stimulated into emitting their stored light-signal by means of illumination with infrared light. The most notable of these is SrS:Eu, Sm, which was studied as a dosimeter by Antonov-Romanovsky et al. (3). Fading was found to be severe at room temperature, and to be a function of the dose, so that interpretation of results is difficult. Sanborn et al. (79) have revived interest in this phosphor. Their preliminary results indicate that 1 mR of Co^{60} γ radiation is detectable. A fading loss of 40% of the signal was found to occur shortly after a γ-ray exposure was completed, but the phosphor was relatively stable after that. The above-mentioned dependence of fading upon the size of the exposure was not reported. Sanborn et al. incorporated their phosphor into a solid transparent plastic block for ease of handling and elimination of phosphor response to mechanical shock or deterioration by the atmosphere.

While the storage properties of this phosphor at present leave much to be desired, nevertheless this and other optically stimulable phosphors deserve additional study. The fact that they need not be heated during readout allows them to be permanently potted in hydrogen-bearing plastics, which may allow considerable enhancement of fast-neutron sensitivity, as well as convenience in handling.

CONCLUSIONS

Silver-activated phosphate glass as a radiophotoluminescent dosimeter has several advantages. It is commercially available from several sources, along with suitable fluorimeters. Its accuracy in the form of miniature rods has been subjected to criticism, but in larger blocks 1-2% reproducibility is obtainable. Temperature sensitivity during exposure and readout, and postirradiation buildup of fluorescence (especially in the low-Z glass), provide problems in achieving this accuracy. Recent improvements in reader design and glass quality have extended the usable range down to 100 mR or even lower. The low-Z glasses, particularly, may be shielded to give good energy-independence of the response per roentgen, although the directional dependence may then become a problem.

The thermoluminescent phosphors calcium fluoride, lithium fluoride and calcium sulfate all are very promising systems for dosimetry. For clinical and radiobiological applications LiF is the system of choice because of the excellent energy independence of the response per roentgen (or per rad in tissue). LiF of thermoluminescent quality is available from several commercial suppliers, and suitable readout equipment is available from two or more companies. The usable range extends down to about 10 mR and is linear to a few hundred roentgens, above which supralinearity begins. This effect, and the

[15] At present by Controls for Radiation, Inc., Cambridge, Massachusetts; and, Madison Research and Development Laboratories, Inc., Madison, Wisconsin.

presence of significant damage to the responsiveness of the phosphor when exposures over 4×10^4 R are given, are limitations on its applicability, but are not serious for most medical or radiobiological uses.

$CaSO_4$:Mn is especially useful where its severe time-fading can be taken into account and very small exposures are to be measured. It can be readily manufactured by published techniques.

CaF_2:Mn is a stable, sensitive phosphor providing good reading reproducibility and a very wide linear range of response vs exposure, and which can be reliably manufactured by published methods. It is nearly stable against γ-ray damage up to 10^8 rad. Its response per roentgen is more dependent upon quantum energy than is LiF or $CaSO_4$, and requires shielding to reduce it to negligible levels. It generally requires packaging for use below about 1 R, to eliminate spurious gas effects.

Developments in thermoluminescent dosimetry systems are proceeding more rapidly now than for any other type. Significant further improvements may be expected to result, with respect to the known phosphors and probably other thermoluminescent materials as well.

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