Thermochimica Acta 52 (1982) 245–254
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

A NEW INSTRUMENT FOR THERMOLUMINESCENCE RESEARCH

DONALD B NUZZIO *

Chemistry Department, Rutgers University, Newark, NJ 07102 (U.S A)

(Received 2 July 1981)

ABSTRACT

A new instrument has been developed to obtain glow curves from ceramic and polymeric materials using commercially available instrumentation This instrument allows for the simultaneous recording of a material's light emission and enthalpic change as a function of temperature Initial data have been obtained on quartz samples A microcomputer system has also been constructed to facilitate data handling Data from the light emission of a sample can be directly stored on floppy disk storage, recalled, analyzed, and plotted

INTRODUCTION

Thermoluminescence (TL) is the light energy of a crystalline substance that is released on heating. Normally, when a material such as quartz has been exposed to any type of ionizing radiation, electrons within that material are promoted to the conduction band. Many electrons fall back to the valence band immediately, but some of the electrons become trapped in places known as electron traps. These traps are normally due to defects or impurities within the crystal lattice. When this material is heated, enough thermal energy is imparted to the system to empty the traps. Once the electrons are released from their respective traps, they can then fall back to the valence band by one of several routes [1–5]. The light emitted, which is associated with the electron's return to the valence band, is proportional to the amount of radiation the material received. The recording of light emitted from a material as a function of increasing temperature is known as a glow curve.

The construction of a reliable thermoluminescence instrument from commercially available equipment is the subject of this paper. The following criteria were considered in the assembly of this new research tool. The instrument had to be able to produce reproducible glow curves from the same sample (especially the position of the peak temperature). This particular feature is lacking in most commercially available thermoluminescence instrumentation, especially those for personnel dosimetry. The instrument had to be able to handle isothermal applications as well as sub-ambient and reduced-pressure investigations. If the instrument were to be used

---

* Present address: Ortho Pharmaceutical Corporation, Raritan, NJ 08869, U S.A

to monitor TL in polymers, it should also be able to record any enthalpic changes simultaneously with the light emission. Currently, an instrument does not exist which could perform all of these tasks. Although the use of a thermal analyzer for thermophotometry equipment is not new, the use of the DuPont 990 system with modification is new and unique.

A microcomputer was used to process and manipulate all data.

The application of thermoluminescence in the investigation of geological [6], archaeological [7], and polymeric [8] materials is well documented. Thus, an instrument with such versatility would be useful in the investigation of any thermoluminescent material.

This study describes the construction and application of this new and unique instrument.

EXPERIMENTAL

General equipment

The DuPont 990 Thermal Analyzer was used with a modified 910 Differential Scanning Calorimeter (DSC); see Fig. 1 for general equipment layout and data flow. The DuPont 990 was used to supply accurate sample temperature information as well as programmed linear heating rates (0.5–100°C min^{-1}).

The light measuring system consisted of an EMI Gencom Model 9824A Photomultiplier Tube (PMT), selected for low dark current. The PMT was enclosed in an

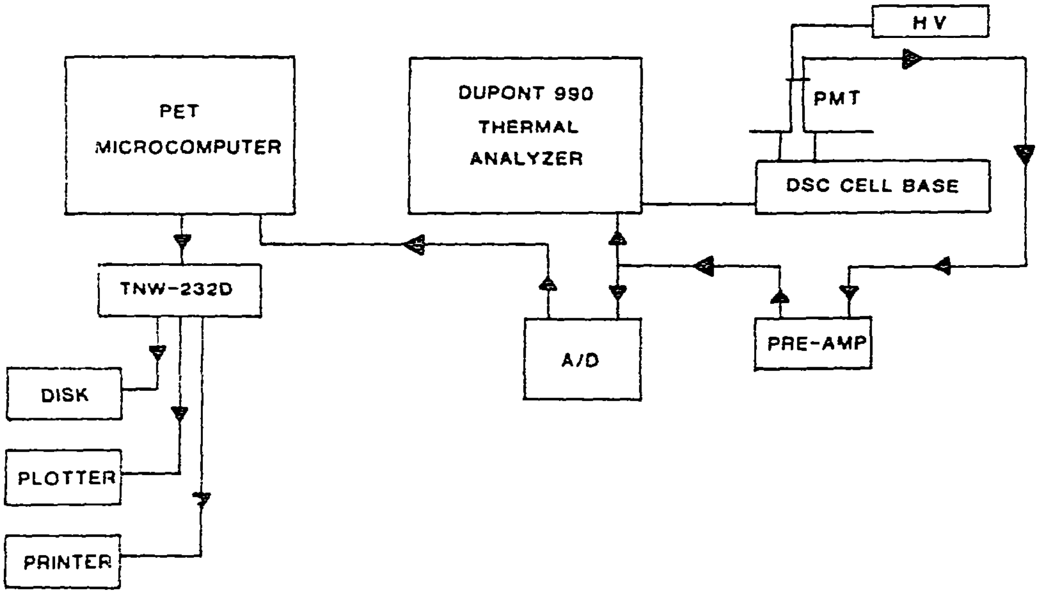

Fig 1 Block diagram of thermoluminescence instrument. Arrows indicate signal/data flow.

EMI Gencom RFI/QL-30F housing (see Fig. 2). The PMT was chosen for its maximum sensitivity in the blue (390–420 nm), which is typical for the thermoluminescence emission of quartz [9, 10]. Included in the light measuring system were filters which absorb heat and minimize the typical black body radiation encountered at high temperatures (i.e. 400°C). The constatin disk within the DuPont DSC cell is an excellent black body source at high temperatures. Thus a Schott, KRG-3 heat absorbing filter, thickness 2.92 mm, and a Hoya type CM-500 filter, thickness 3.28 mm, were used in combination to minimize the effect of heat and black body radiation; see Fig. 3 for the combined spectral response curve of these filters. The spectral response curve was recorded using a Varian Super Scan 3 Ultraviolet/Visible Spectrophotometer equipped with an integrating sphere. This sphere allows for

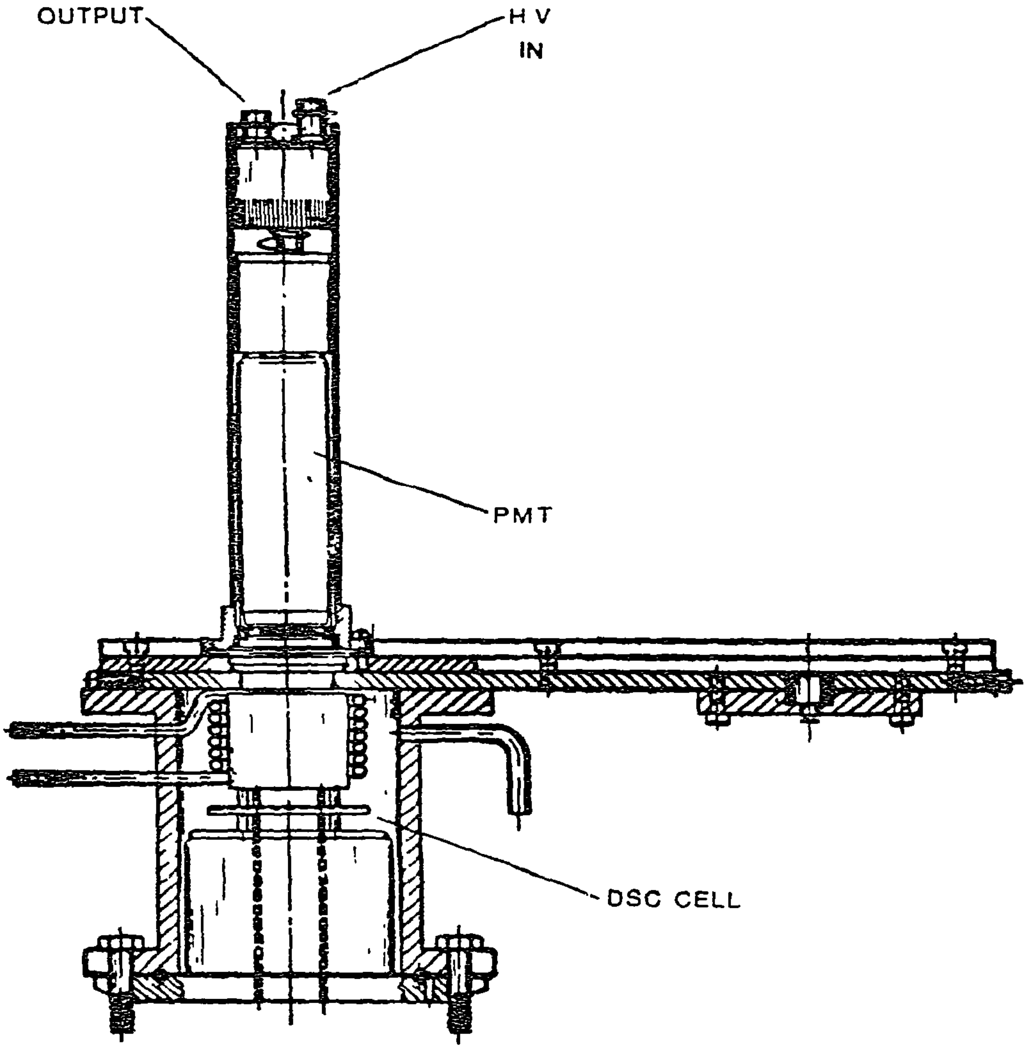

Fig 2. Cut-away diagram of light measuring unit. The DuPont DSC cell is shown with cooling coil in place. Note, vent port is to the right of DSC cell. PMT assembly is over sample chamber ready for a measurement The reference light source is to the right of the PMT assembly

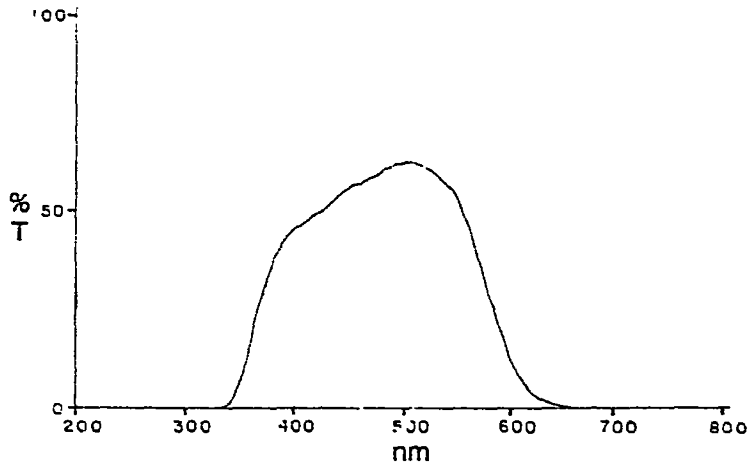

Fig 3 Spectral transmission response curve for the combined KRG-3 heat absorbing filter and the CM-500 filter Scanning rate, 50 nm min^{-1}

diffuse light measurements and collects all scattered light produced from a sample (i.e. filters). The PMT was powered by an EMI Gencom High Voltage d.c. Power Supply Model 3000R and was usually operated at −600 V.

Amplification system

The light signal produced by the sample and sensed by the PMT was amplified in one of two ways The first system consisted of an RCA BiMos Operational Amplifier Model Ca-3160AE; see Fig. 4. The Operational Amplifier (Op Amp) has a typical input current of 5 pA. The assembled system has a sensitivity of 1 nA V^{-1} and was equipped with silicon diodes on the input to protect the Op Amp from

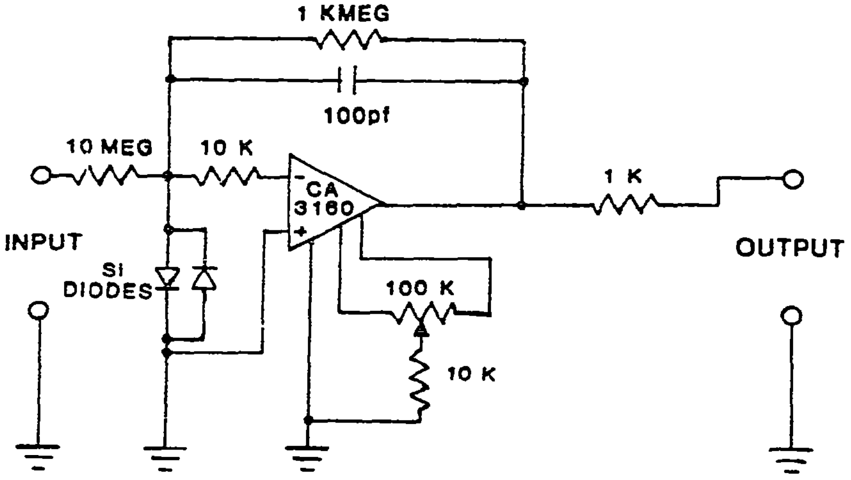

Fig 4 Schematic diagram of low sensitivity amplification circuit. This circuit was used in preliminary runs on unknown samples Note input protection on Op Amp

possible saturation due to samples with high light emissions. This circuit was used in the preliminary investigations of unknown materials.

If the light emission of a material was low, such as those expected in archaeological samples, the second system was used; see Fig. 5. This system consisted of an Analog Devices Ultra Low Bias Current Varactor Bridge Operational Amplifier Model 310J. This particular amplifier has an input bias current of ± 10 fA maximum. Because of its increased sensitivity, extreme care was employed in its installation. Proper shielding and grounding of cables was mandatory for optimum performance. This Op Amp System had a sensitivity of 100 pA V^{-1}. Extreme care had to be taken when using this unit since no input protection to the Op Amp was employed. The use of protection diodes and resistors decrease this unit's sensitivity.

Both amplification systems required a ± 15 V d.c. power supply which was furnished via an Analog Devices Dual Output Power Supply Model 920, ± 15 V d.c., 200 mA.

Thus a wide range of light emitting materials was accommodated by these two systems.

The amplified signal can be sent to the DuPont 990's recorder system, thus allowing for the analog representation of the glow curve. Otherwise, the signal can bypass the 990's recorder and be sent to an Analog to Digital Converter (A/D) for digitalization and later data manipulation; see Fig. 1. Alternatively, the signal can be displayed on the 990's recorder and sent to the A/D Converter simultaneously, thus allowing an experiment to be followed in real time as well as storing the data in the microcomputer's memory.

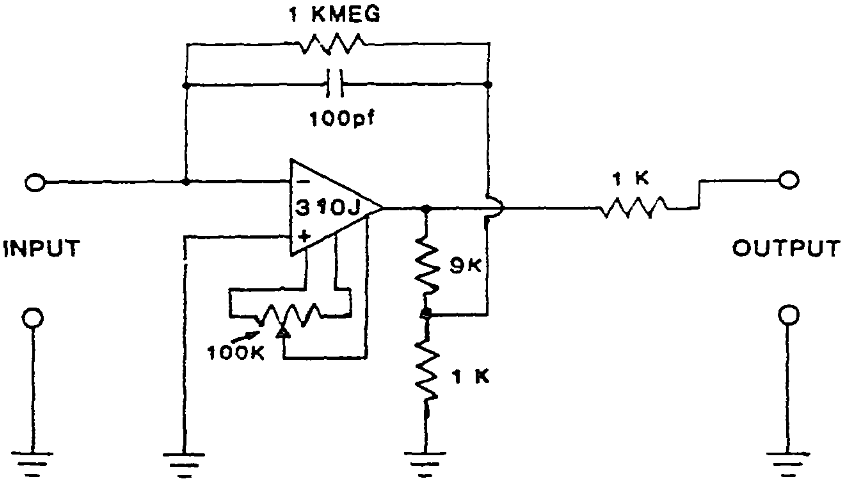

Fig. 5 Schematic diagram of high sensitivity amplification circuit Used with samples which emit low light levels Note no input protection on Op Amp

Analog to digital converter and microcomputer system

The analog to digital (A/D) conversion of the amplified light emission was accomplished using an Analog Devices 12-Bit Successive Approximation Integrated Circuit A/D Converter Model AD572AD. This unit has a typical conversion time of less than 25 μsec. The rate of analog to digital conversion of the amplified signal was software selectable (1–25 data points sec^{-1}). The A/D converter was powered by an Analog Devices Dual Output Power Supply Model 920, ±15 V d.c., 200 mA. Five volts were supplied to the A/D converter from the same power supply using a Texas Instruments voltage regulator chip model TI-7805C.

Once the data was digitalized, it was sent to the microcomputer system. The microcomputer used was a Personal Electronic Transactor (PET) Model 2001 32K version equipped with 4.0 Basic, made by Commodore. The PET microcomputer has a parallel user port which consists of four input ports (labeled PA-0 to PA-3) and four output ports (labeled PA-4 to PA-7). In order to process a 12-Bit piece of information, a gating system was devised in order to read a 12-Bit number into the four input ports. The three gating chips used were Texas Instruments Model 74125 which were sequentially activated by the PET to read a 12-Bit number; see Fig. 6. The chips were powered using +5 V from the voltage regulator chip.

Once the data has entered the microcomputer's random access memory (RAM), the data can be analyzed by a basic program. The data can either be sent directly to a disc memory system or analyzed immediately with the output sent to a plotter or printer.

The PET microcomputer was connected to a TNW232D IEEE to RS232 interface module which allowed it to communicate to other peripheral devices. The peripheral

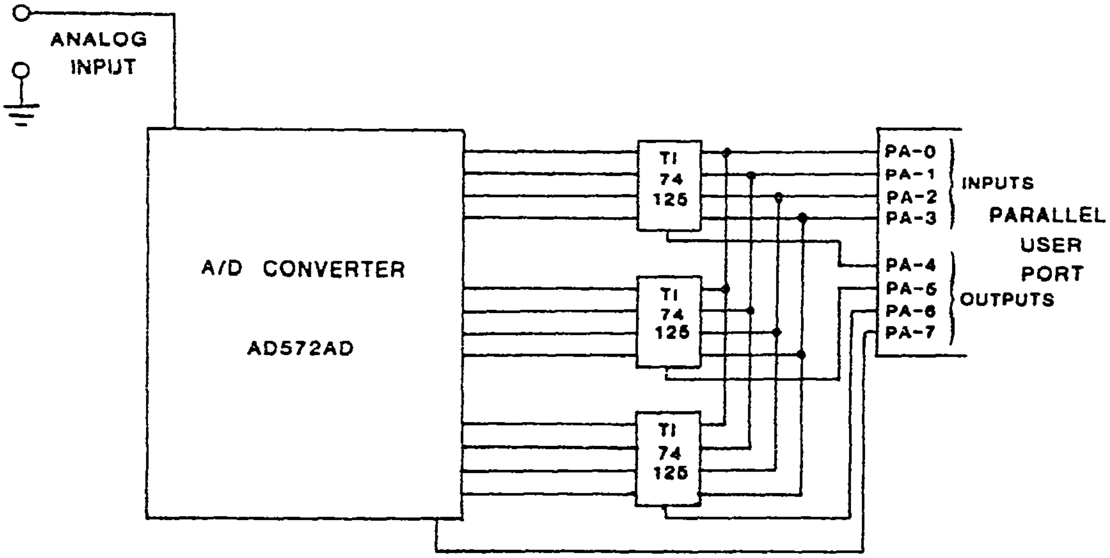

Fig 6 Block diagram of Analog to Digital Converter TI 74125 Gating chips used to gate 12-bit digital information into 4 input ports of the microcomputer

devices used were the Commodore Model 8050 1 megabyte dual floppy disc drive, the Houston Instrument Model DMP-8 Digital Plotter and a DEC III Terminal used as a printer set up at 1200 baud. Once the data was collected, it could be processed many ways. Since the PET microcomputer is programmable in Basic, a minimum amount of effort was required to construct programs for data analysis.

Instrument calibration

After a warm-up period of approximately one hour, a method to calibrate the PMT was devised to insure instrument reliability from day to day. This was done by sliding the PMT assembly over the reference light source which was a Harshaw Chemical Reference Light Source with an activity of 0.5 μCi. The light source contains the radioisotope carbon 14, on barium carbonate, sandwiched between two calcium fluoride europium crystals. This reference light source provided a constant low level light emission by which the instrument was calibrated. Prior to recording the light emission from any sample, the calibration of the instrument was checked using the reference light source. A particular set of operating conditions was chosen for this purpose. If any deviation on the recorded light output was noted on the recorder, ±0.5 V, no further measurements were made until the source of error was found.

This particular system also allows for the monitoring of the PMT as a function of time, thus checking any decaying characteristics the PMT might be experiencing

RESULTS AND DISCUSSIONS

Using the system described, this instrument is capable of following many types of light emission phenomena as a function of temperature (isothermal or increasing temperature). Presently, a detailed study of the effects of iron oxide diffusion on the glow curve of low quartz is in preparation [11] using this instrument. A typical glow curve of low quartz 4 months after being irradiated with 10,000 rads of ^{60}Co gamma radiation is shown in Fig. 7. A summary of peak temperatures on successive glow curves of low quartz irradiated with ^{60}Co as described can be seen in Table 1. This table illustrates the instrument's precision in obtaining reproducible data. The CA-3160AE Op Amp system and a high voltage setting of 500 V were used to record this glow curve. A heating rate of 50°C min^{-1} was also selected. Because of the simplicity of this system, sensitivity can be increased or decreased depending on the material under investigation. By changing the voltage on the PMT as well as changing the feedback resistor in the Op Amp circuit, the instrument can accommodate a wide range of light emissions.

In order to record a typical glow curve, one must allow the instrument, especially the PMT, to warm up. The instrument is then checked using the reference light source as previously described. Once this is done, a sample is weighed in a typical aluminum pan used for DSC. The sample is then placed in the DSC cell and the

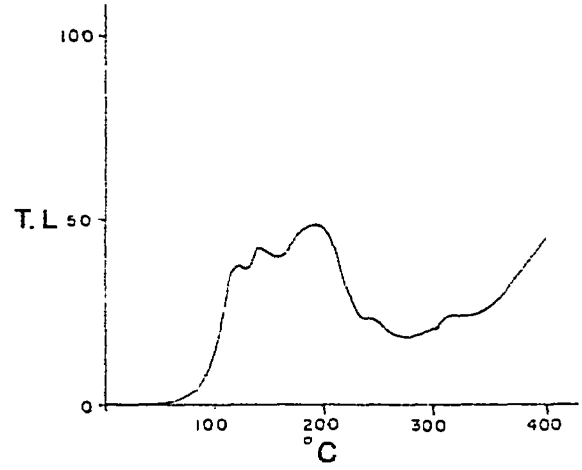

Fig 7 Typical glow curve of α-quartz Heating rate 50°C min^{-1}

PMT assembly positioned over the sample area. The sample area is purged with nitrogen which has been passed through an Oxisorb filter. The sample compartment is purged for 5 min at a rate of 100 cm^3 min^{-1}. The heating rate is selected on the 990's temperature programmer and the heat button depressed to engage the heating program. As the sample is being heated, the light emission is displayed on the y axis. The x axis displays sample temperature. While the glow curve is recorded on the 990's recorder (analog presentation), the A/D converter is simultaneously digitalizing the analog signal for later data processing.

When the glow curve has been recorded, the PMT assembly is slid back to the intermediate position (position between sample and reference light source). The sample is removed from the sample chamber and the flow of nitrogen increased to facilitate cooling. A flow of cold water is passed through the cooling coil in order to cool the DSC cell in preparation for the next sample.

If an isothermal experiment is to be carried out, the temperature is set on the 990's programmer and the sample is placed in the sample chamber. The "iso" button

TABLE 1

Instrument reproducibility
Sample α-quartz

Sample	Peak temperature[a] (°C)
1	195
2	194
3	194
Mean	194 3
Std Dev	0 6

[a] Only major peak emission reported

on the 990 is depressed after the PMT assembly is moved into position. The x axis is placed in the time mode and the light emission at a specific temperature is recorded as a function of time. Thus, kinetics involved in specific trap emptying can be studied [12].

If reduced pressure work is of interest, several small additions can be added to the present instrument to accommodate these measurements. A rubber O-ring would be placed under the PMT assembly and a clamp arrangement applied to the assembly after the sample has been loaded in the sample chamber. A valve on the vent tube must also be installed to provide an air-tight system. The sample chamber can now be evacuated through the vacuum port on the DSC Cell Base after which a glow curve under reduced pressure may be recorded [13,14].

The present instrument can also be used for low temperature light emission experiments. This instrument would be especially useful in the investigation of polymers where many transitions occur below room temperature [15]. Any subsequent light emission associated with an enthalpic change could be recorded simultaneously. The instrument would be used in manner similar to that in ambient conditions; however, liquid nitrogen would be allowed to fill the cooling coil around the DSC cell. This would cool the cell to the desired temperature (no less than −100°C) and the desired temperature program begun.

Future work in these other areas are presently under investigation and will be the subject of another publication.

CONCLUSION

Thermoluminescence has many applications in the fields described. With the advent of a low cost modification of commercially available instrumentation, more research in this area of thermal analysis would become practical. Many analytical laboratories which possess thermal analysis instrumentation could inexpensively examine their own materials for thermoluminescence.

REFERENCES

1 F Urback, Akad Wiss Wein Ber, 139 (1930) 363.
2 J T Randall and M H F Wilkins, Proc. R Soc (London), Ser A, 184 (1945) 366
3 C B Lushchik, Dokl Akad Nauk SSSR, 101 (1955) 641
4 A Halperin and A A Braner, Phys Rev, 117 (1960) 408
5 R H Bube, J Phys Chem, 57 (1953) 785
6 D J McDougall, Thermoluminescence of Geological Materials, Academic Press, New York, 1968
7 S Fleming, Thermoluminescence Techniques in Archaeology, Clarendon Press, Oxford, 1979
8 M Dole, The Radiation Chemistry of Macromolecules, Vol 1, Academic Press, New York, 1972, p 193
9 W L Medlin, J. Chem Phys, 38 (1963) 1132
10 M David, C M Sunta and A K Ganguly, Indian J Pure Appl Phys, 15 (1977) 201
11 D.B Nuzzio, to be published

12 F.S W. Hwang, J Geophys Res, 77 (1972) 328.
13 W W. Wendlandt Thermochim. Acta, 35 (1980) 247
14 W.W. Wendlandt, Thermochim Acta, 35 (1980) 255.
15 M. Dole, The Radiation Chemistry of Macromolecules, Vol 1, Academic Press, New York, 1972, p. 218