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The use of LEDs as an excitation source for photoluminescence dating of sediments

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In this note we describe the configuration and performance of a simple and low-cost photo-excitation module currently under development, which makes use of high intensity light emitting diodes. The unit is designed as an adaption for a conventional high temperature oven used in TL dating; the characteristics of the device, and its potential for application to PL dating is assessed.

Introduction

The use of low energy photons in stimulating higher energy luminescence for probing the mechanisms of luminescence and the nature of defects is well established (see Curie, 1963). Huntley et al (1985) showed that such anti-Stokes emission, excited by 514 nm laser radiation, could potentially be used as a tool for dating, an observation which was quickly taken up by others (Smith et al, 1986; Rhodes, 1988). Godfrey-Smith et al (1988) found that IR radiation could excite luminescence in both feldspar and quartz, also demonstrating that this could be excited in feldspar using an LED (880 nm; FWHM 100nm). Although excitation with such low energy photons was unexpected, Hütt et al (1988), who had also studied this effect, found that the mechanism of electron eviction was phonon-assisted. In a detailed study of K-feldspar, they measured the low energy photo-stimulation spectrum ($2.4 < h\upsilon < 1.1$ eV) whilst monitoring the high energy luminescence emitted from the sample. The stimulation spectrum displayed several resonant excitations peaking at 1.29, 1.33, 1.43 and 2.25 eV, leading to direct optical ionization of the centre at 2.5 eV. The lower energy resonances were interpreted as transitions from the ground state to a sequence of excited states, where electrons could be elevated to the conduction band by phonon absorption. The thermal trap depth of these defects was also determined, and found to be of the order of 2 eV, suggesting suitability for dating. This was substantiated in their paper by preliminary age determination results for a number of sediment samples. We have developed the above observations by assessing the suitability of LEDs emitting at 950 nm (FWHM 100nm) for use in practical dating applications.

Experimental Details

A variety of LED's are commercially available, broadly being grouped into the very high intensity infra-red sources (based on GaAs), or near IR/red (AlGaAs), to the lower intensity visible devices (green/red) based on GaP. They are made by most of the major electronic device manufacturers and, in the UK, prices range from £0.3 to £2.5 each. We have so far used both green and infra-red diodes, having considerably more success with the latter. Results are described for the use of 15 mW, 950 nm (1.3 eV) GaAs LEDs (Telefunken TSUS 5402).

Sixteen diodes were arranged in a circular array around the sample, mounted at 30° to the horizontal. Luminescence emitted perpendicularly through this ring was monitored with the same PM tube as used in the TL measurements, with the addition of Schott BG38 filters to reject the scattered IR radiation. This simple set-up is shown in figure 1. The dimensions were chosen for low light loss when exciting samples deposited on 10mm diameter discs. Beam uniformity across a section of such a disc is shown in fig 2, as determined by optical bleaching of charge trapped in a 1x1x0.1mm crystal of geological K-feldspar.

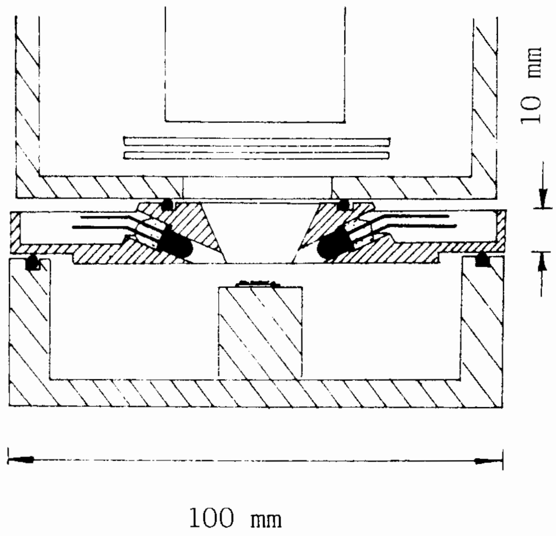


Figure1
Cross-section of the diode array described in the text. The device is used as an adaptation to an existing TL oven (lower part of the figure), inserted below the photomultiplier tube (top). The 16 LEDs are fixed with silicone sealant to cut out stray light, and allow the oven chamber to be evacuated, if necessary. Typical dimensions of the module are shown.

The LEDs were connected in parallel to a current limiting DC power supply. The initial light output of the LEDs (as measured by radiation scattered from a "white" paper disc) was in proportion to the current, up to the maximum ratings of the devices. If the current was limited to less than 1 A (the recommended typical operating value), then the light output was proportional to the power supplied (figures 3a&b). However, for higher values of current, a transient was observed upon switching on (figure 3c&d), settling down to an equilibrium output after approximately 10 s. For lower

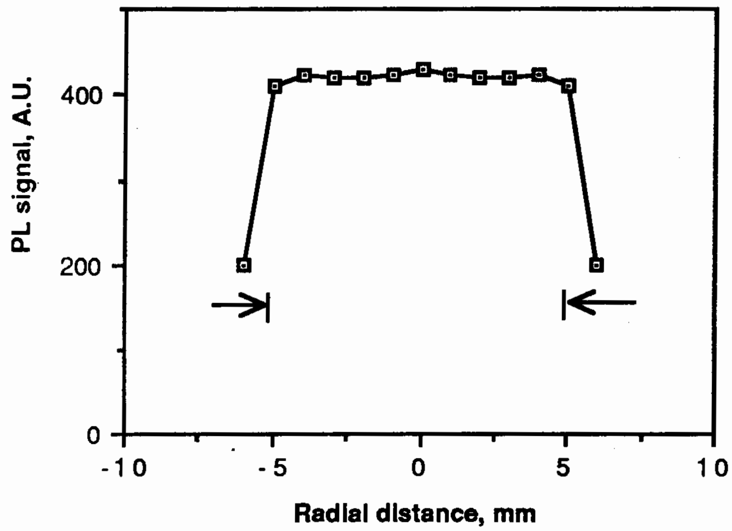


Figure 2
Radial uniformity of the excitation source of the 16 LEDs aranged in a circular array, as shown in figure 1. The markers indicate the dimensions of the sample discs used.

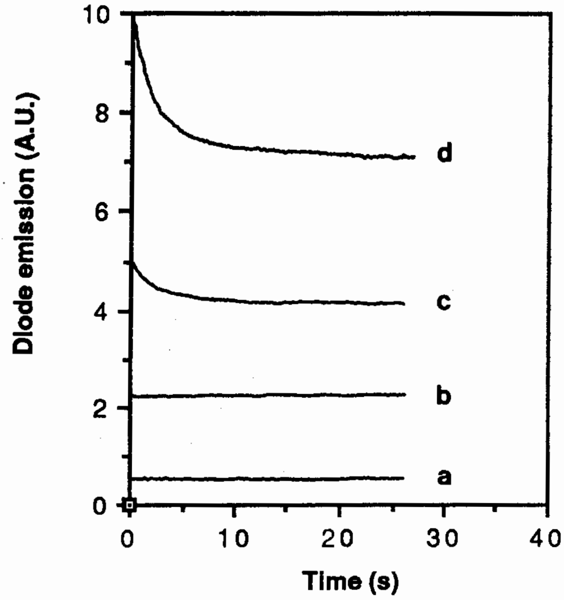
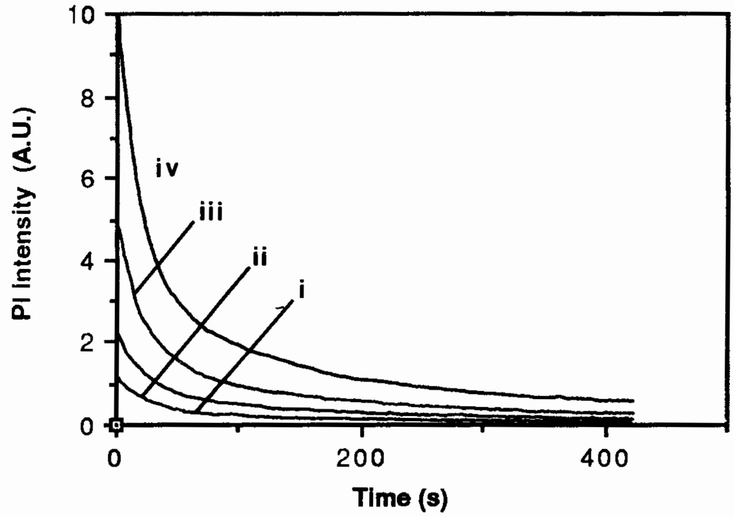
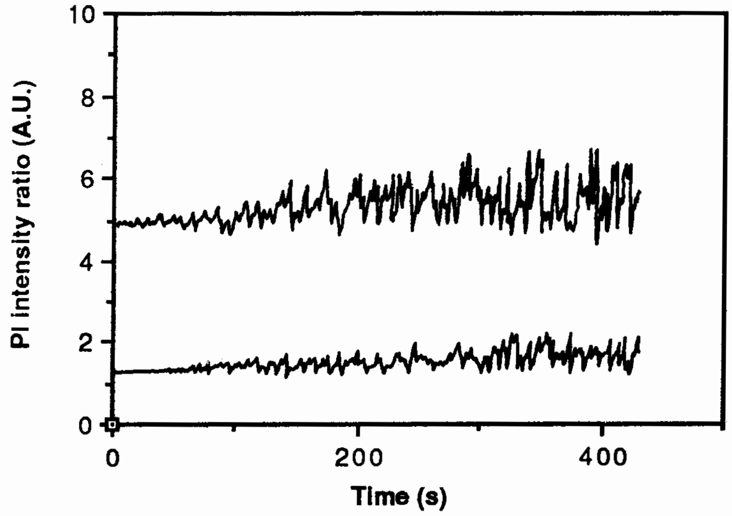


Figure 3
Light output characteristics of the LEDs with increasing current throughput; a)0.25A(1.2V); b) 0.85A (1.4V); c) 1.55A(1.6V); d) 3.0A (2.0V). Values are for the array of 16 diodes.

Figure 4



a) Time decay characteristics of IR stimulated luminescence of K-feldspar having received various beta doses (see text). The initial count-rate of curve iv was 50 kcps.



b) Ratio of the PL curves ii and iv shown in a), with respect to curve i.

values of current, this equilibrium was as stable as the power supply (in our case, constant to within experimental measurement determination of ±0.5%). For practical dating applications, the current was limited to be at or below 1 A, yielding estimated excitation powers at the sample of less than 60 mW cm^{-2}. It is also noted that these devices have good switch on/off characteristics which make them suitable for pulsed operation.

Discussion

Using infra-red radiation to induce ionization of traps stable over archaeological times, requires a more complex mechanism than direct photo-eviction, and one possibility is discussed by Hutt et al (*ibid*). These processes may therefore only be found in a limited number of materials. The samples we have so far studied which showed IR stimulated emission (where the laboratory doses administered were typical for archaeological material) were Na and K-feldspars, and pink quartz. By far the strongest luminescence, however, is stimulated in the K-feldspars, and it is in the dating of these minerals that we envisage the device to be most practicable.

The preliminary results of dose-response tests performed using 90-150 μm sedimentary K-feldspar are shown in figure 4. Using a simulation dose of 1.6 Gy and a regeneration procedure, values of ED of a) 1.58 ± 0.01 Gy and b) 1.55 ± 0.03 Gy were obtained. The basis for these calculations were a) using the ratios of the PL intensities measured at 1 s intervals between 0 and 10s after switch on, and b) using the ratios of the integrated PL intensities to a time where the intensity was less than 2% of the initial value. The difference in the results obtained using these two methods of analysis is, in this case, not significant. However, analysis of the decay curves for the above and other sedimentary feldspar samples has revealed that the form of the decay may be dose dependent. This is most easily seen when comparing the values of integrated PL (normalised to equal dose) plotted against time. Where such differences are significant, values of ED obtained as a function of exposure time (see Rhodes, 1988) using PL intensity ratios will show a systematic variation.

The real potential of the PL module in dating young sediments is still under assessment, but initial results look encouraging. One sample examined was a fine-grain marine sediment, extracted from Samsø, Denmark, (carbon dated to 3760+/-95 bc (K-4002)). XRD analysis indicated the presence of quartz and equal quantities of plagioclase and K- feldspars. By using bleach-regeneration (using bleach wavelengths longer than 500 nm) and additive dose techniques for measurement of palaeodose, apparent ages of 3870 ±750 and 4920 ± 690 BC respectively were produced when using the integrated curve as a measure of trapped charge (fading tests are in progress). Although these initial results are encouraging, further investigations are clearly needed.

Conclusion

The characteristics of 950 nm emitting diodes for use as PL excitation sources makes them potentially suitable in dating applications. A particular advantage of using IR compared with visible excitation is the reduced problem of rejecting excitation wavelengths, where a blue/uv biassed photomultipliers are employed for detection. The potential also exists for using a set of LEDs emitting at different wavelengths (or dual colour LEDs) mounted in the same array for selectively exciting individual mineral components within a polymineral sample. However, if this is to be successful, much more needs to be known about the charge trapping and transfer mechanisms in the relevant minerals.

Acknowledgements

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PI Reviewer's Comments (Ann Wintle)

The use of cheap LEDs for stimulating luminescence in minerals extracted from sediments opens up a new field of study, which, when carried out in parallel with TL studies, will lead to a greater understanding of the basic mechanisms. This study developed from the very interesting paper given by Galina Hütt at the Cambridge meeting in 1987.