

PHOTOTRANSFERRED THERMOLUMINESCENCE OF CaWO_4 CRYSTALS

A. Shmilevich, D. Weiss, R. Chen and N. Kristianpoller
Tel Aviv University
Raymond and Beverly Sackler Faculty of Exact Sciences
School of Physics and Astronomy
Tel-Aviv, 69978, Israel

Abstract — The PTTL of CaWO_4 crystals was studied after exposure to X or β radiation at RT, and subsequent illumination with UV light at LNT. The main PTTL peaks appeared at 195 and 280 K, while TL peaks recorded at 165, 280, 340 and 400 K. TL could be excited only by band to band transitions, but PTTL could also be stimulated with photon energies smaller than the band gap. The trap responsible for the 340 K TL peak acts as a reservoir for the phototransfer. The PTTL and TL emission spectra showed a main broad 500 nm band composed of components at 490 and 520 nm. The XL and PL showed maxima at these wavelengths, indicating that the same luminescence centres are responsible for the PTTL as for TL, XL and PL emissions. The dependences of the PTTL intensity on the β dose and on that of the stimulating UV were both sub-linear.

INTRODUCTION

The photoluminescence (PL) and thermoluminescence (TL) of CaWO_4 crystals have previously been studied by various authors (e.g. Refs 1, 2). The TL was normally excited by X rays or by UV irradiation into the long wavelength tail of the absorption edge near 4 eV. In a recent work the TL was also excited by vacuum UV (VUV) radiation⁽³⁾. In the present work the phototransferred thermoluminescence (PTTL) of CaWO_4 crystals was studied in the temperature range between 80 and 300 K. The results were compared to those obtained for the TL and PL in the same crystal. The dependence of the luminescence efficiency on the temperature was measured between LNT and RT. Effects of optical and thermal bleaching as well as the dose dependences of the PTTL intensities were also investigated.

EXPERIMENTAL PROCEDURE

The nominally pure CaWO_4 crystals were obtained from RCA Laboratories. The X irradiations were performed with a W tube (40 kV, 15 mA) and the β irradiations with a ^{90}Sr source of a $1.5 \text{ Gy}\cdot\text{min}^{-1}$ dose rate. For the VUV irradiations a 1 m normal incidence monochromator (linear dispersion 0.83 nm/mm) and a 1000 W hydrogen arc lamp were used. The photon flux of the incident light was monitored by a sodium salicylate screen. For the illumination in the non-vacuum UV region a 150 W Xe lamp was used. For the TL and PTTL measurements the samples were kept in a vacuum cryostat; the heating rate was $20 \text{ K}\cdot\text{min}^{-1}$. The emission and excitation spectra were taken with Aminco-Bowman/2 luminescence spectrometer.

EXPERIMENTAL RESULTS AND DISCUSSION

For the PTTL measurements the samples were first irradiated at RT by X, β or high energy UV radiation, then cooled to LNT and illuminated with monochromatic low energy UV or visible light ($\lambda < 500 \text{ nm}$). PTTL peaks appeared at 195 and 280 K (Figure 1, curve A). For some PTTL measurements the X irradiated samples were heated to 340 K and then illuminated with UV light at LNT; but no PTTL peaks could be recorded in this case. For comparison the TL induced by X or short UV irradiation at LNT was measured and essentially the same TL was obtained in both cases (Figure 1, curves B and C). The main low temperature TL peaks appeared at 165 K and 280 K; no TL peak was recorded at 195 K. The excitation of TL by VUV radiation has recently been reported for CaWO_4 crystals; these TL excitation spectra showed a sharp increase toward lower

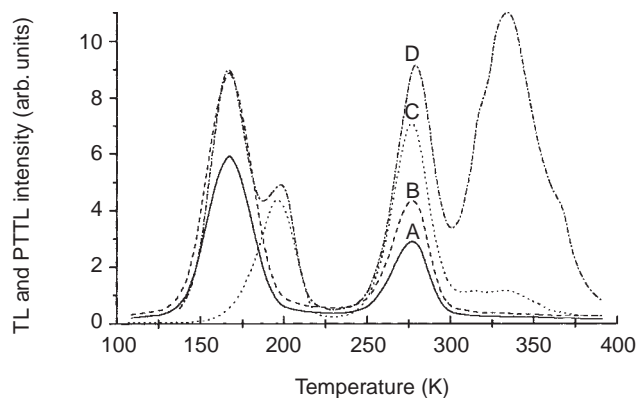


Figure 1. TL and PTTL glow curves: A, TL after 10 min 190 nm illumination at LNT; B, TL after 5 min X irradiation at LNT; C, PTTL after 5 min X irradiation at RT and subsequent 10 min illumination with 360 nm at LNT; D, PTTL after 5 min X irradiation at RT and subsequent 10 min illumination with 190 nm at LNT.

wavelengths up to about 160 nm, but no distinct maximum has been shown⁽³⁾. The excitation spectra of the VUV induced 165 K TL peak measured here showed a main maximum at 170 nm and a weaker maximum at about 130 nm (Figure 2). Only a very weak TL was excited with wavelengths between 200 nm and the absorption edge of CaWO₄ near 300 nm and no TL could be excited with wavelengths longer than 300 nm. A similar excitation spectrum was recorded for the 280 K TL peak. After X or β irradiation at RT the main peaks appeared at 340 and 400 K. After X or β irradiation at RT and subsequent UV illumination at LNT with wavelengths shorter than 300 nm, the 165 and 280 K TL peaks as well as the 195 K PTTL peak appeared (Figure 1, curve D). Sayer and Souder⁽¹⁾ have previously reported that after LNT irradiation of CaWO₄ crystals, doped with monovalent Cu or Na impurities, two TL peaks appeared at 160 and 260 K. After irradiations at temperatures between 140 and 180 K, the intensity of 260 K TL peak rapidly decreased with increasing temperature⁽¹⁾. An analogous, but less pronounced behaviour has now been observed in our nominally pure samples. This behaviour in the nominally pure tungstate crystals may possibly be due to a casual monovalent impurity, which becomes unstable above 140 K and causes an annihilation of the electron centre responsible for the 280 K TL peak. A similar behaviour has previously also been reported in semiconducting diamonds and has been attributed to an instability of an intermediate energy level in a multistage transition process⁽⁴⁾.

After X irradiation at RT and subsequent UV illumination at LNT the dependence of the PTTL intensity on the wavelength of the stimulating light was measured in the spectral range between 300 and 600 nm and showed an excitation maximum near 360 nm. The PTTL could also be efficiently stimulated by shorter wavelengths, but the experimental results have shown that the 195 K peak could not directly be excited solely by ionising radiation, by either short UV light or by X rays.

The thermal stability of the various traps was investi-

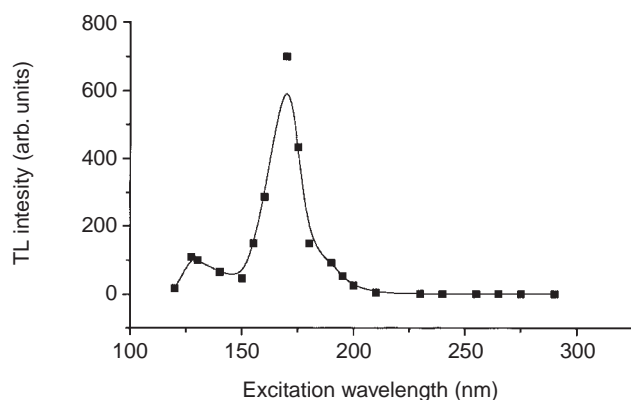


Figure 2. TL excitation spectrum (results were normalised for the incident photon flux).

gated by annealing to gradually increasing temperatures. The fact that after X irradiation at RT and heating to above 340 K no PTTL peak could be recorded, suggests that the 195 K peak is due to a phototransfer process from the trap, responsible for the 340 K TL peak to shallower traps. The finding that this phototransfer could be stimulated with low energy UV and even with visible light up to about 500 nm, and not solely by ionising UV or X radiation, indicates that the phototransfer is due to a tunnelling process rather than to a transition via the conduction band.

The thermal activation energies of various TL and PTTL peaks were evaluated by the initial rise method⁽⁵⁾ and values of 0.17, 0.55 and 0.58 eV were obtained for the 165, 280 and 340 K TL peaks respectively. The same values were achieved after VUV as after X excitation. The activation energy of the 195 K PTTL peak was found to be 0.24 eV. About the same results were obtained by the symmetry method⁽⁶⁾. The 340 K TL peak is composed and therefore the symmetry method could not be applied. The results are summarised in Table 1.

The PTTL and TL emission spectra showed both a main broad band near 500 nm, composed of two components at 490 and 520 nm (Figure 3). The XL and PL

Table 1. Thermal activation energies of the TL and PTTL peaks evaluated by the initial rise and symmetry methods.

TL peak (K)	PTTL peak (K)	Act. energy by initial rise method (eV)	Act. energy by symmetry method (eV)
170	—	0.17	0.18
—	200	0.24	0.21
280	—	0.55	0.54
—	285	0.55	0.55
340	—	0.58	—

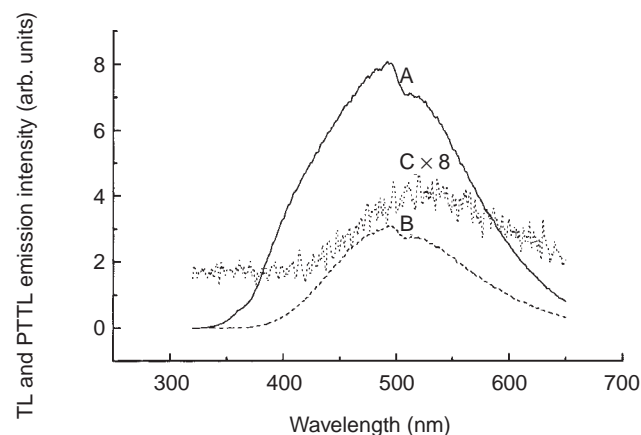


Figure 3. Emission spectra recorded at: A, 165 K TL peak; B, 280 K TL peak; C, 195 K PTTL peak.

also showed maxima at these wavelengths, indicating that the same luminescence centres are responsible for these PTTL, TL, XL and PL emissions. Additional bands at 415 and 360 nm appeared in the PL and XL only.

An excitation maximum for the 360, 490 and 520 nm PL emission bands was recorded at 275 nm but the 415 nm emission had a different excitation maximum at 255 nm. The broad blue luminescence band, which appeared at 420–440 nm has generally been attributed to a WO_4^{2-} complex anion centre; while the green emission near 530 nm has been ascribed to a WO_3 defect centre^(3,7). The temperature dependence of these PL emission bands was now measured during cooling from RT to LNT. The 415 nm band was found to decrease, while the intensity of the broad 490–520 nm increased with decreasing temperature.

Effects of optical bleaching of the TL were investigated. The X irradiated samples were exposed for 30

min to a monochromatic light beam in the spectral range between 180 and 600 nm and TL was measured. The photon flux of the incident light was kept constant for the various wavelengths. TL intensities were compared with those obtained after only X irradiation. In Figure 4 the efficiency (η) of the optical bleaching induced by the monochromatic light beam is given as a function of the wavelength: $\eta = 1 - I/I_0$, where I_0 and I are the TL intensities before and after exposure to the bleaching light. It can be seen that 200 nm light was most efficient for the optical bleaching of the TL.

The dose dependences of the PTTL intensities on the β radiation as well as on the stimulating UV light were measured. In Figure 5 the dependence of the PTTL intensities on the β dose is given in a log-log plot and the slope was about 0.7. The dependence on the dose of the stimulating UV light was also sublinear, with a slope of 0.3 only.

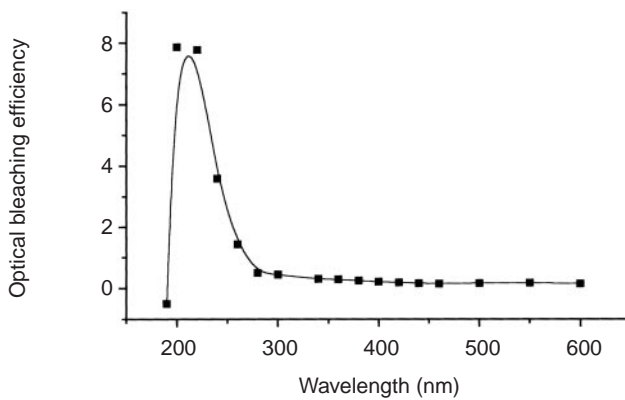


Figure 4. Wavelength dependence of optical bleaching efficiency of TL. The TL was measured after 10 min excitation with 190 nm and subsequent 30 min illumination with various wavelengths at LNT (results were normalised for intensities of the Xe lamp at these wavelengths).

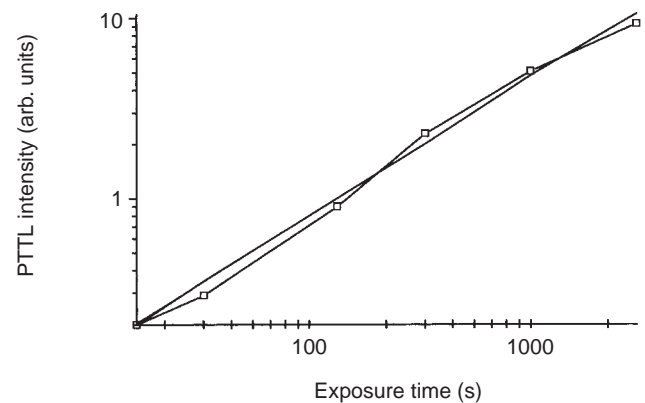


Figure 5. Dependence of the PTTL intensities on the dose of the β irradiation. The periods of the β irradiations at RT were gradually increased while the stimulation with UV light was kept constant (10 min, 360 nm at LNT). The dots represent the experimental results and the solid line shows a best fit of the regression.

REFERENCES

1. Sayer, M. and Souder, A. D. *On the Origin of Defect States in Calcium Tungstate*. *Can. J. Phys.* **47**, 463–471 (1968).
2. Grasser, R. and Scharman, A. *Luminescent Sites in CaWO_4 and $\text{CaWO}_4:\text{Pb}$ Crystals*. *J. Lum.* **12/13**, 473–478 (1976).
3. Muerk, W., Nikl, M., Mihorova, E. and Nitsch, K. *A Study of Electron Excitation in CaWO_4 and PbWO_4 Single Crystals*. *J. Phys. Condens. Matter.* **9**, 249–256 (1997).
4. Winer, S. A. A., Kristianpoller, N. and Chen, R. *Effects of Thermoluminescence Excitation in Semiconducting Diamonds*. In: *Luminescence of Crystals, Molecules, Solutions* Plenum Publ. Corp. 473–477 (1972).
5. Garlick, G. F. G. and Gibson, A. F. *The Electron Trap Mechanism of Luminescence in Sulfide and Silicate Phosphors*. *Proc. Phys. Soc.* **60**, 574–590 (1948).
6. Chen, R. *On the Calculation of Activation Energies and Frequency Factors from Glow Curves*. *J. Appl. Phys.* **40**, 570–585 (1969).
7. Grasser, R., Scharman, A. and Strack, K. R. *On the Intrinsic Nature of the Blue Luminescence in CaWO_4* . *J. Lum.* **27**, 263–272 (1982).