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2002 J. Phys.: Condens. Matter 14 7065

(http://iopscience.iop.org/0953-8984/14/29/308)

Institute of Physics Publishing Journal of Physics: Condensed Matter

J. Phys.: Condens. Matter **14** (2002) 7065–7069 PII: S0953-8984(02)36353-7

Phototransferred thermoluminescence of PWO and PWO:Y single crystals

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Received 29 April 2002, in final form 10 June 2002
Published 11 July 2002
Online at stacks.iop.org/JPhysCM/14/7065

Abstract

The phototransferred thermoluminescence (PTTL) of PWO and PWO:Y crystals was studied in the range of 30–300 °C. From the experiments, one can conclude that in PWO crystals there are abundant traps and that some traps must be very deep. Visible light (blue, green and red) illumination can change the distribution of the trapped charges—namely, some charges trapped by deep traps can be transferred to shallow traps. These traps above room temperature are in practice detrimental to the light yield and its stability. Doping with Y^{3+} is a good way to reduce the number of these traps, as can be concluded from the γ-irradiation-induced thermoluminescence and PTTL curves. This paper provides us with some clues as regards how to enhance the stability of the light yield, which is an important requirement for PWO in high-energy physics detection applications.

1. Introduction

In the past few years, luminescence and scintillation properties of $PbWO_4$ (PWO) crystals have been investigated extensively, because PWO has been selected as the new scintillator for used in the Compact Muon Solenoid (CMS) of the Large Hadron Collider (LHC) at CERN [1].

It is well known that the emission spectrum of the PWO crystal is composed of several sub-bands which are distributed throughout almost the entire visible region (350–750 nm). The luminescence properties of PWO are very sensitive to its structure and to its defects. Samples produced using different growth technologies and different post-treatments can show significant changes in the spectral components and other properties. In general, WO_4^{2-} (or Pb^{2+}), $(WO_3 + F)$ and complex defects such as $(Pb^{3+} + O_k + F^+)$ are considered as blue, green and red luminescence centres, respectively [2]. But the origin of the green luminescence is most probably '$WO_4 + O_i$' centres, as proposed by our group [3–5].

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The complicated character of the emissions from PWO scintillators is due to the fact that both the regular lattice and a defect-based centre contribute to the optical properties—especially the scintillation properties. They are sensitive to defects in the crystal, which can form during the crystal growth, post-treatment and doping with other ions. In order to improve the optical properties of PWO, doping with trivalent rare-earth ions (RE^{3+}) such as La^{3+}, Y^{3+}, Gd^{3+} [6–9] and annealing are often used. The existence of the defects can strongly affect the scintillation properties. This is because the traps produced by the defects will take part in carrier transfer processes which influence the temperature dependence of the PWO luminescence.

Thermoluminescence (TL) curves below room temperature (RT) have provided much useful information about the shallow traps which can influence the scintillation kinetics by releasing trapped charges, subsequently taking part in the radiative recombination process. Spectral components of green or even red emission were found in the TL, which shows that the charges released from traps recombine with some defect centres. The TL above RT shows the existence of deep traps which will induce a very slow component, which will be detrimental in high-energy physics detection applications.

The phototransferred thermoluminescence (PTTL) arises from trapped charges transferred from deep traps to shallow ones due to visible light illumination. Illumination with light can lead to a redistribution among the traps. This method makes it easy to find the deep traps, which are usually difficult to detect due to the temperature quenching phenomenon at such high temperatures. Because of the possible existence of very deep traps, we measured the PTTL of PWO and PWO:Y crystals after visible light illumination. This paper shows that there are such filled deeper traps, by means of the effect of phototransfer to shallower traps observed in measurements of PWO TL.

2. Experimental procedure

The single crystals of PWO and PWO:Y (100 mol ppm) used in the experiments were grown by the Bridgman method using the initial materials WO_3, PbO and Y_2O_3 (for doping with Y^{3+}) with purity not less than 99.99%. The samples were polished to slices $10 \times 10 \times 1$ mm^3 in size. TL curves were recorded as the temperature rose linearly from 30 to 300 °C at a rate of 10 °C s^{-1} using a QS-3500 TL Reader (HARSHAW Company). A ^{60}Co source was used to irradiate the samples. A tungsten–halogen lamp with an appropriate light filter was used as the illumination source (blue, green and red).

3. Results and discussion

The TL curves of the two samples after γ-irradiation ($\sim$10 kGy) are shown in figure 1. The TL of the undoped sample peaks at 60 and 193 °C. The TL of the PWO:Y sample is much weaker than that of the undoped one. The suppression of the TL peaks at about 60 °C was also reported for doping with the other rare-earth trivalent ions Gd^{3+} [10] and La^{3+} [11, 12] of PWO. Such suppression can be ascribed to the compensation of the defects in PWO by doping with trivalent ions. Although the kinds of defect responsible for various TL bands are not definitely clear yet, the defects are certain to be induced by the vaporization of raw materials (PbO and WO_3) and consequently to form anion and cation vacancies which are electron and hole traps respectively. The γ-irradiation-induced TL of the two samples were recorded (figure 1). Then the samples were kept at a constant temperature of 300 °C for 20 min to ensure that all the electrons or holes captured by the traps below 300 °C had been released. Then the temperature returned to RT ($\sim$28 °C), the samples were illuminated by visible light for 15 min and this was

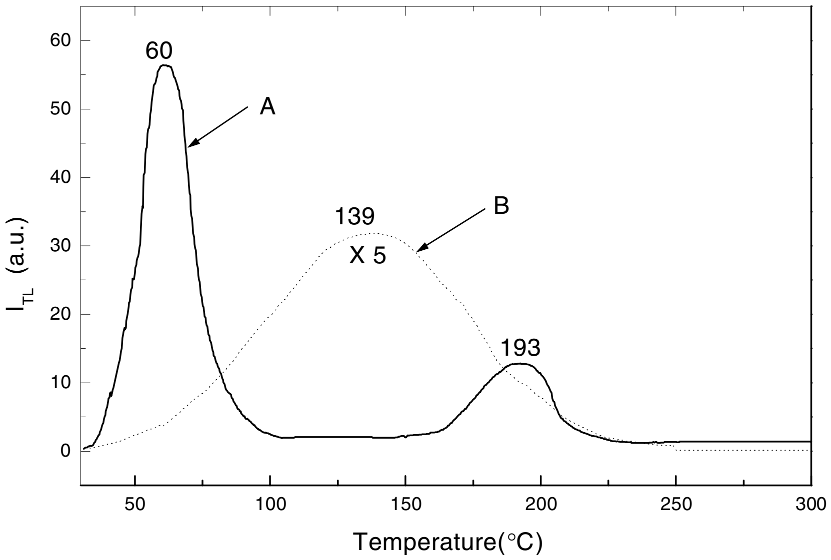

Figure 1. TL of PWO (curve A) and PWO:Y (curve B) after γ-irradiation with a dose of 10 kGy at 30 °C.

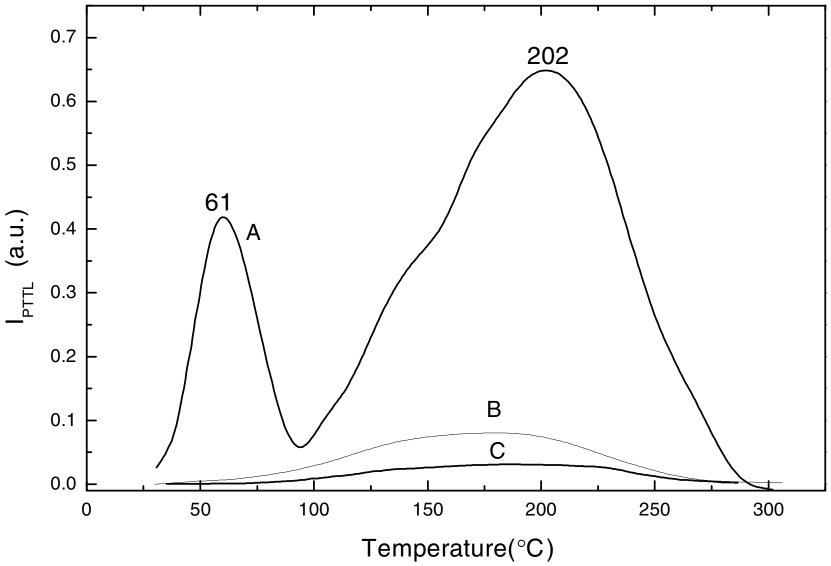

Figure 2. PTTL of PWO crystal after different types of visible light illumination at RT. A (blue), B (green), C (red).

followed by the TL measurement. Figures 2 and 3 show PTTL curves, because the samples were not irradiated by γ-rays but illuminated by visible light. Most importantly, the intensity of the PTTL for the two samples is much lower than that of the γ-irradiation-induced TL. The PTTL of undoped PWO maintains two TL bands peaked at 61 and 202 °C after blue illumination but shows only one (rather weak) TL band at about 180 °C after green or red illumination. The PTTL of PWO:Y shows only one band peaking at 168 °C for blue and green

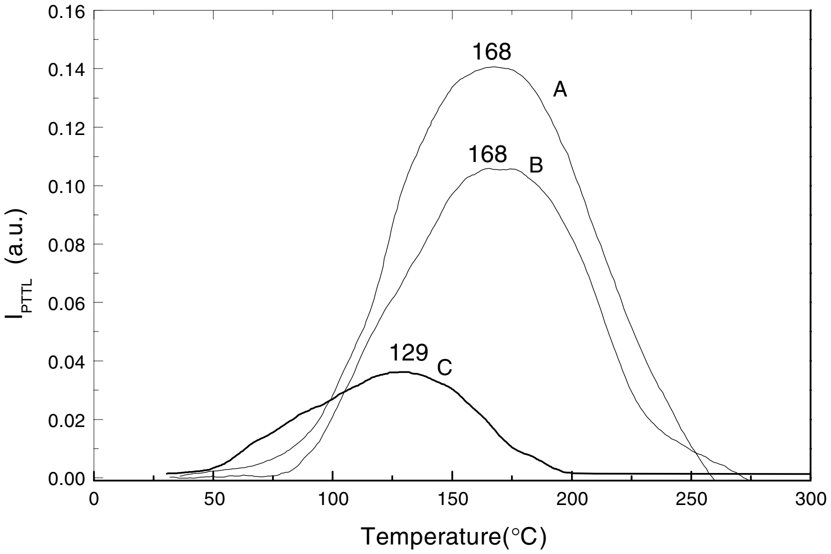

Figure 3. PTTL of PWO:Y crystal after illumination with different types of visible light at RT. A (blue), B (green), C (red).

light illumination and one at 129 °C for the red light illumination; the positions of the peaks also shift to lower temperature compared with the case of γ-irradiation-induced TL.

In the PWO crystals there are many traps with various depths and some traps may be very deep; the corresponding TL peaks should be higher than 300 °C. At such high temperatures, TL measurement will become very difficult because of the temperature quenching effect. The PTTL plays an important role in helping us to understand the very deep traps. During the γ-ray irradiation, the very deep traps of PWO crystal were also filled up but the trapped charges are difficult to release below 300 °C.

The energy of visible light mentioned above (1.8–2.8 eV) is much lower than the band gap of PWO ($E_g \sim 4.3$ eV), so it is impossible to excite the electrons from the valence band into the conduction band. The role of visible illumination is to change the distribution of the trapped carriers from deep traps to shallow ones. The redistribution is by two possible mechanisms. In the first one, the illumination can stimulate the trapped charges in the deep traps into the conduction band; subsequently some charges will recombine at luminescence centres and some others will be retrapped by some shallow traps. In the second one, the light can transfer the charges directly from the deep traps to shallow ones without them coming through the conduction band. The effects of visible light with different wavelengths are not the same, due to their different quantum energies.

From the TL curves, one can evaluate the depth of shallow traps to be about 0.6–0.9 eV using the formula (1) proposed by Chen [13]:

$$\begin{aligned} &E = (ckT_m^2/\omega) - 2kT_m \\ &\omega = T_2 - T_1; \qquad c = 2.52 + 10.2(\mu_g - 0.42); \qquad \mu_g = (T_2 - T_m)/(T_2 - T_1) \end{aligned} \tag{1}$$

where k is Boltzmann's constant. T_m is the temperature at the maximum. T_1 and T_2 are the low and high half-intensity temperatures.

For the first of the possible processes mentioned above, the depth of deep traps is somewhat less than the energy of the visible light (2–3 eV), which may be explained in the configuration coordinate model. In the case of the second process mentioned above, the depth of the deep traps is greater than the depth in the first case. In fact, the depth of the deep traps in the second case is the sum of the depth of deep traps in the first case and the depth of the shallow traps. For the second case, the traps are very deep. We still think it is a possibility, because the defects in PWO are very complicated.

In general, the intensity of the PTTL for undoped PWO crystal is stronger than that for the PWO:Y crystal. For the undoped PWO, the effect of blue light is dominant and those of green and red light are slight. However, in the case of the PWO:Y the effects of blue and green light are stronger than that of red light.

The effect of illumination is very important in practice. Long-term stability of the light yield is one important requirement for scintillators used in high-energy physics experiments. The trapped charges can be thermally elevated to the conduction band and consequently participate in the luminescence process, which is one of the reasons for light yield fluctuation. Usually the traps in TL below 300 °C have a lifetime of several days to several years at RT, which could substantially influence the stability of the light yield when using PWO as a scintillator in the CMS. Deep traps responsible for the TL above 300 °C have a very long release time. Such traps have no direct effect on the fluctuation of the light yield. But when PWO crystals are exposed to visible light, the charges in very deep traps will be phototransferred to shallow traps and so influence the light yield.

For PTTL, decreasing the number of traps in PWO crystal is important in practice whether the traps are shallow or deep. Doping with the trivalent rare-earth ions Y^{3+} is good for reducing the trap concentration. The results show that γ-irradiation-induced TL and PTTL are both reduced upon doping with Y^{3+}.

4. Conclusions

The PTTL curves of PWO and PWO:Y show that some very deep traps must exist in PWO crystals and that visible light (blue, green and red) illumination can cause trapped charges to transfer from very deep traps to shallow ones. Doping with Y^{3+} can reduce the concentration of traps and enhance the stability of the light yield.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (59732040, 19774053).

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