The traps effect on temperature dependence of luminescence from PbWO$_4$ crystals

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Abstract

In this Letter the influence of traps on the temperature dependence of PbWO$_4$ (PWO) luminescence is reported in 110–350 K. The electrons trapped at some defects can contribute to the luminescence at special temperature due to the thermally elevation. This conclusion can be drawn from the experimental results of radioluminescence (RL) and thermoluminescence (TL) in the same temperature range. The TL measurements show there are four TL peaks with the first-order kinetic process from 110 to 300 K. The order of kinetics was got though isothermal TL decay curves. The evaluation of trap parameters of TL was obtained using the method of fit. The values of $\frac{s}{C^2} \exp\left(-\frac{E}{kT}\right)$ acquired by the two methods were coincident.

1. Introduction

In the past few years, luminescence and scintillation properties of PbWO$_4$ (PWO) crystals were investigated extensively because PWO has been selected as the new scintillator used for the Compact Muon Solenoid (CMS) of the Large Hadron Collider (LHC) at CERN [1]. Comparing with other scintillators, e.g., NaI(Tl), the PWO scintillator has many unique properties such as fast luminescent decay time, high density, short radiation length and high radiation hardness, etc. The emission of PWO is mainly composed of blue bands (400–440 nm) from the regular lattice (WO$_4^{2-}$) and green bands (480–520 nm) ascribed to defect centers associated ‘WO$_3 + F$’ [2] or WO$_4 + O_i$ (interstitial oxygen) centers [3–5].

The complicated character of the emission from the PWO scintillator is due to the fact that both regular lattice and a defect-based centre contribute to its optical properties. Especially, the scintillation properties are sensitive to defects in the crystal, which can form during the process of growth, post-treatment, and doping with other ions. In order to improve the optical properties of PWO, doping with trivalent rare earth ions such as La$^{3+}$, Y$^{3+}$, Gd$^{3+}$ [6–9] and annealing in air or oxygen are often used. By doping with Nb, Y, La, Lu ions [10], the PWO crystals produced by the

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Bogoroditsk Technochemical Plant in Russia has obtained better optical properties, such as a better optical transmission near the absorption edge, at least a factor 2 more radiation than undoped ones. In practice, whatever annealing or doping of other ions, the purpose in essence is to control or adjust the defects of PWO which can harm the properties of scintillation. Meanwhile, such methods using dopant will also induce inevitably other defects such as impurity point defects. The existence of defects can strongly affect scintillation properties for example, the traps formed by the defects will take part in carrier transfer processing which influence on the temperature dependence of PWO luminescence. The relationship between thermoluminescence (TL) and scintillation mechanisms has been studied by other groups [11]. It was found that the TL traps can be responsible for the slow decay processes at the green emission centers [11].

In this Letter, the temperature dependence of radioluminescence (RL) and TL of PWO as well as their relationship are reported. In order to verify the effect of traps on the RL, two reverse directions of changing temperature are used. From the data of TL, one can get information on both localized traps and recombination luminescence centers. The relation between the temperature dependence of the RL and TL is discussed.

2. Experimental

The crystals used in our experiments were grown using the Bridgman method with the initial materials WO₃ and PbO with purity not less than 99.99% by Shanghai Institute of Ceramics. The samples were polished to slices 10 × 10 × 1 mm³ in size.

The temperature dependence of RL in the range of 110–350 K was measured using two reverse direction of temperature change, namely, from 350 K down to 110 K and from 110 K up to 350 K. In the experiment the excitation source was an X-ray tube (50 kV, 30 mA) for the RL measurement. The TL measurements were performed from 100 to 300 K by X-ray irradiation at 95 K for 2 min and then a linear heating with rate 0.25 K/s. A TC-100U temperature controller with different program was used for temperature control in the detection. The isothermal decay curves were measured at the peaks of TL, which is an effective method to determine the kinetics order of TL.

3. Experimental results and discussion

The temperature dependence of RL for the PWO sample from 110 to 350 K is given in Fig. 1(a) and (b) corresponding to heating-up the sample from 110 to 350 K and cooling-down the sample from 350 to 110 K, respectively. From the curves, it can be founded that above 150 K the intensity was quickly thermally quenched which is the common feature in both curve (a) and (b). The first report on radioluminescence of PWO in function of temperature appeared in 1994 [12]. The result of temperature quenching is similar to previous reports [12,13]. But it must be noted that in the curve (a) there is a shoulder at about 200 K and an unusual enhancement peaking at 260 K which is some different from curve (b). In fact, these features also appeared in the previous experimental results of other group [13], but it was not noticed and nobody has discussed it. The main aim of this Letter is to analyze the effects of trap on the temperature dependence of PWO luminescence. Additionally, it is very interesting that the structure of deviation from the normal exponential law at about 200 and 225 K.
also appeared in the temperature dependence of luminescence decay time of PWO crystal, which were attributed to the effects of trap states in the PWO crystal [14]. Supposing the decay of the luminescence intensity with raising temperature (Fig. 1(b)) only due to the thermal quenching, the luminescence intensity \( I(T) \) with function of temperature can be described as
\[
I(T) = \frac{I(0)}{1 + A e^{-\Delta E/kT}},
\]
where \( I(0) \) is the luminescence intensity at 0 K, \( \Delta E \) is activation energy, \( k \) is the Boltzman constant, \( A = \rho_{nr}/\rho_r = \text{constant} \), \( \rho_{nr} \) and \( \rho_r \) are the nonradiation- and the radiation-transition probability, respectively.

The fit of the experimental result with formula (1) is given as the curve (c) in Fig. 1. One can see that the experimental curves (a) and (b) mainly accord with the fit, but for curve (a) there is a deviation from standard thermal quenching behavior in the interval 230–300 K. The TL glow curve is shown in Fig. 2. The curve shows that the sample has four TL peaks at 135, 191, 207 and 245 K. In order to determine the order of kinetics, the isothermal decay curves at the peaks 135, 207, 245 K were recorded and shown in Fig. 3. If the isothermal decay curve is satisfied with exponential decay law, namely the formula (2), the corresponding TL process will be first-order kinetics
\[
I(t) = I_0 e^{-Pt},
\]
\[
\ln I(t) = \ln I_0 - Pt,
\]
\[
P = s e^{(-E/kT)},
\]
where \( P \) is the thermo-release probability, \( I_0 \) is the initial intensity, \( s \) is the frequency factor. It can be found from formula (2) that at fixed temperature the value \( P \) is constant for certain trap so the formula shows the exponential decay law with time. The formula (2) can be also described as formula (3). There is a linear relationship between \( \ln I \) and \( t \) with a slope as \( P \).

The isothermal decay curves can be linearly fitted with the formula (3), given in Fig. 3 which shows the linear relationship between \( \ln I \) and \( t \) for the three decay curves and indicates that they all belong to first-order kinetics. First-order kinetics of TL means the released electrons will never be trapped again while they must recombine with holes at luminescence centers to arise luminescence.

For the general-order (not first-order) case, the TL decay can be presented as formula (4) which is not simple exponential [15]
\[
\frac{I(t)}{I_0} = 1 + n_0^{n-1} (n - 1)s' e^{(-E/kT)t},
\]
where \( n \) (not equal 1) is the order of kinetic, \( n_0 \) is the initial concentration of trapped carriers.
In order to evaluate the trap parameters of TL, namely $E$ (activation energy) and $s$ (frequency factor), the TL glow curve of PWO in Fig. 2 was fitted as four first-order peaks based on the Randall–Willkins formula [16] described as follows:

$$I(T) = \sum_{i=1}^{4} n_0 s_i \exp(-E_i/kT),$$

$$\times \exp[-(s_i/\beta) \int_{T_0}^{T} \exp(-E_i/kT) \, dT],$$  \hspace{1cm} (5)

where $I$ represents the TL intensity; $T$ the temperature; $T_0$ the initial temperature; $\beta$ the heating rate; $n_0$ the initial trapped carriers concentration; $k$ the Boltzmann constant. The trap parameters are summarized in Table 1. The values $s \times \exp(-E/kT)$ from the fitting formula (5) are consistent with them obtained from the isothermal TL decay curves described by formula (3). So the evaluation of the $E$ and $s$ is credible.

From the TL glow curve, one can find the trap effects on the temperature properties of RL. It can be concluded that the electrons captured by traps with various depths can take part in the luminescence process in certain temperature region, corresponding to the trap depth. At low temperature, under the excitation with X-ray, the electrons excited into conduction band will mostly recombine with holes at the luminescence centers to arise static state emissions, but still some electrons will be trapped subsequently and stored by electron traps with various depths. When the sample is heated, the stored electrons at lower temperature are thermally released into conduction band and thereby recombine at luminescence centers with holes creating additional luminescence, inducing the increase of the RL intensity at some temperature corresponding to TL. The process participated by thermo-released electrons depends on two factors. Firstly, there are enough amount of trapped electrons, which indicates the sample must be excited at low temperature and some electrons have been stored at traps. Secondly, the thermo-release probability is high enough. Such phenomena only occur when the temperature is so high that it is energetically close to the activation energy of the trapped electrons. In this situation, the luminescence intensity is high enough to be detected by the experimental setup. With increasing temperature up to over activation energy the trapped electrons are all evacuated, there will be no trapped electrons to influence the RL intensity. So the shoulder at about 200 K and the peak in 230–280 K of the curve (a) in Fig. 1 can be easily interpreted as the trap effect because of the existence of the TL peaks in the corresponding temperature region. If the assumption is right, then when the way of changing sample temperature is from high to low rather than from low to high, there is no trap effects appear. The hypothesis has been proved by the experimental curve (b) in Fig. 1, in which the trap effect was not observed. In the measurement of curve (b), the temperature decreased from 350 to 110 K, there were no trapped electrons to participate in the luminescence process. In fact, at higher temperature, if the electrons are trapped by traps but immediately released so that a dynamic equilibrium is quickly established and no electron can be stored at the traps.

4. Conclusion

In PWO single crystals, the electrons trapped at some defects can contribute to the luminescence at special temperature due to the thermal release. This conclusion can be drawn from the comparison with experimental results of RL at different ways of changing $T$ (heating and cooling) and TL curves in
the same temperature range. The TL measurements show there were four TL peaks which belong to a first-order kinetic process from 110 to 300 K.

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