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Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

A method for kinetic analysis and study of thermal quenching in thermoluminescence based on use of the area under an isothermal decay-curve



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ARTICLE INFO

Article history:

Received 30 October 2013

Received in revised form

24 February 2014

Accepted 27 February 2014

Available online 11 March 2014

Keywords:

Isothermal decay-curve

Area

Thermoluminescence

Kinetic analysis

Quartz

 α -Al₂O₃:C

ABSTRACT

A method for kinetic analysis based on the use of the temperature-dependence of the area under an isothermal decay-curve is reported. The technique is not limited to use of areas corresponding to two measurement temperatures. The method is best suited to calculation of the activation energy in the case of first-order kinetics, and suitable limiting cases of general-order kinetics, and has been demonstrated using measurements made on quartz. In addition, the dependence of the area on the measurement temperature can be used to study thermal quenching. This has been illustrated using isothermal decay curves obtained from quartz and α -Al₂O₃:C. A key advantage of the method is that it can apply in cases which cannot easily be described by the Mott-Seitz model. Various results found using the method compare favourably with values obtained from conventional methods of kinetic analysis; from the literature, and are consistent with contemporary theory of stimulated luminescence.

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1. Introduction

Phosphorescence is the decay of thermoluminescence with time at a constant temperature. Thermoluminescence (TL) is an extensively documented method for monitoring changes in concentrations of point-defects in materials [1,2]. Its signal typically appears as a temperature dependent set of peaks or a glow-curve with each peak associated with an electron-trapping point defect. More comprehensive details on the dynamics involved in the thermoluminescence can be obtained when the signal is recorded as an emission spectrum to reveal information not only concerning the electron traps but about luminescence sites as well [3–7]. The physical processes involved in the emission of the luminescence can be described with reference to kinetic parameters such as the order of kinetics or the activation energy of a particular electron trap. The range of mathematical methods for analyzing glow-curves is wide [1,2,8–10] with new variations regularly appearing in contemporary literature e.g. [11–13]. In contrast, the analysis of phosphorescence has mostly relied on the use of the shape of its decay-curve.

An alternative method for analyzing phosphorescence that has received only little attention is the use of the area underneath the

isothermal decay curve. McKeever [1] alluded to it. Furetta et al. [14] explored it. The method developed by Furetta et al. [14] is for calculation of the activation energy using phosphorescence subject to first, second and general-order kinetics. In their method, the activation energy is abstracted from the ratio of the area of phosphorescence decay curves measured at two different temperatures. Furetta et al. [14] demonstrated their technique in measurements made on the phosphor, K₂YF₅:Pr³⁺, and obtained results that were in excellent agreement with ones calculated using common means of kinetic analysis such as the initial-rise method.

The method of Furetta et al. [14] however presents two experimental concerns. The first is that the criteria for choosing which pair of temperatures to use is not obvious and the question of whether any pair can produce similar results remains open. The second point is that their method requires that the total area under an isothermal decay-curve be known, which in practical terms, calls for an extended measurement time. The dilemma here is that a prolonged measurement, while necessary and suitable to accurately determine E for an isolated peak, may cause simultaneous loss of signal from several peaks and particularly where such peaks are closely overlapping e.g. [15]. On the other hand, improperly approximating the total area would then inevitably introduce inaccuracies in E .

We report a new method of kinetic analysis based on the use of the temperature-dependence of the area under an isothermal decay-curve. The technique is not limited to use of areas corresponding to

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two measurement temperatures as in the method of Furetta et al. [14]. Our method is best suited to calculation of the activation energy in the case of first-order kinetics. For illustrative purposes only, the method has been applied on phosphorescence from quartz. The technique also allows for the temperature-dependence of the area under an isothermal decay curve to be analysed using glow-curve deconvolution to obtain the order of kinetics and the activation energy. In addition, the dependence of the area on the measurement temperature can be used to study thermal quenching. This has been demonstrated using measurements on quartz and on the ultra-sensitive luminescence dosimeter, α -Al₂O₃:C. The various results found using our technique are compared with values obtained from conventional methods of kinetic analysis as a means to demonstrate the reliability and versatility of the method.

2. Experimental methods

Measurements were made on natural quartz (BDH Ltd, UK) annealed at 800 °C. The quartz was selected for its high sensitivity from a suite of samples used previously [16–19]. Apart from normal kinetic analysis, the sample was also used in studies on thermal quenching as were quartz annealed at 500 °C and α -Al₂O₃:C. All experiments were conducted using a RISØ TL/OSL-DA-20 Luminescence Reader. The luminescence was detected by an EMI 9235QB photomultiplier tube through a 7 mm Hoya U-340 filter (transmission band 260–390 nm). Samples were irradiated *in-situ* at room temperature using a ⁹⁰Sr/⁹⁰Y beta source at a rate of 0.10 Gy s⁻¹. Unless otherwise specified, quartz samples were irradiated to 10 Gy. The thermoluminescence was measured in a nitrogen atmosphere to prevent false signals from air and to improve thermal contact between the sample holder and the heater planchet.

3. General features of thermoluminescence of the main peak

The area-based phosphorescence method to be reported was applied on isothermal decay curves measured at temperatures on the main TL peak of natural quartz annealed at 800 °C for 10 min. In order to assess the efficacy and reliability of this new method, its resultant values are compared with those obtained using a range of alternative ones, reviewed elsewhere [1,2,8–10], comprising the initial-rise, variable heating rate, whole glow-curve method and glow-curve deconvolution methods as well as conventional phosphorescence methods used to analyse isothermal decay-curves by way of their shape. Such a comparative study is necessary as a way of corroborating the various independent calculations. The analyses of the main peak using the complementary methods are presented first. Analyses using the temperature-dependence of the area under isothermal decay-curves then follow.

Fig. 1 shows a glow-curve measured at 5 °C s⁻¹ from a sample of natural quartz irradiated to 10 Gy. The glow-curve consists of at least 3 peaks (as clarified in the inset); the dominant one at about 90 °C as well as secondary peaks at about 200 and 350 °C. For ease of comparison, the various kinetic analyses were performed only on the main peak.

3.1. Order of kinetics

Methods of kinetic analysis are usually valid for certain orders of kinetics and not others. Therefore preparatory to further analysis using the area-method, we investigated the order of kinetics of the peak and confirmed it to be first-order based on the fact that the position of the peak did not shift by more than 2 °C with dose or with pre-heating from 30 to 70 °C.

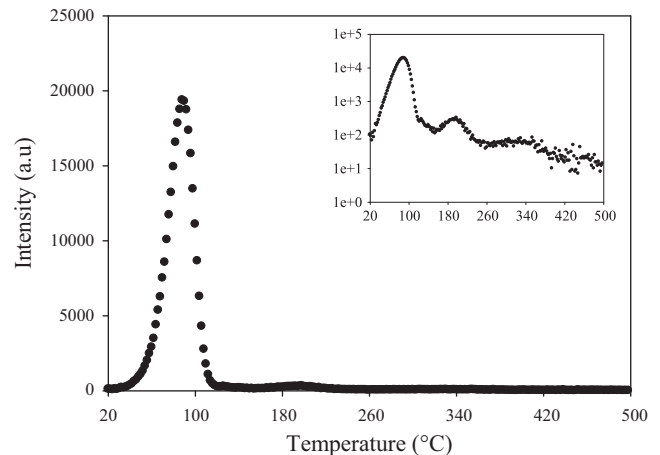


Fig. 1. A glow-curve measured at 5 °C s⁻¹ from a sample of natural quartz irradiated to 10 Gy. The inset, with the intensity on a logarithmic scale, is included to better show secondary peaks above 200 °C.

4. Kinetic analysis using peak position, partial and whole-curve methods

4.1. Analysis using the initial-rise, variable heating rate and whole glow-curve methods

The activation energy was determined using the initial-rise, variable heating rate and whole glow-curve methods as 0.94 ± 0.02 eV, 0.96 ± 0.03 eV and 0.982 ± 0.004 eV, respectively, which are evidently consistent. In addition, the whole-curve method gave $b = 1.1$ which agrees with the earlier conclusion that the peak is of first-order.

4.2. Influence of heating rate on thermoluminescence intensity

Fig. 2 shows the influence of heating rate on thermoluminescence intensity. The intensities, noted as areas under the glow-peak, decrease with heating rate as can also be deduced in the inset. Such a change indicates that the peak in question, the main peak here, is affected by thermal quenching [8].

If it must be that the thermoluminescence corresponding to the lowest heating rate experiences the least amount of quenching, then the area I_u of its glow-peak is related to the subsequent quenched ones I_q measured at higher heating rates through the expression

$$I_q = \frac{I_u}{1 + C \exp(-\Delta E/kT_m)} \quad (1)$$

where E is the activation energy of thermal quenching [8], T_m is the peak position and $C = \nu\tau_{rad}$ where τ_{rad} is the radiative lifetime at absolute zero of temperature and ν is the frequency factor applicable to the non-radiative process [17]. Alternatively, in terms of radiative and non-radiative probabilities A_R and A_{NR} , $C = A_{NR}/A_R$ [20]. The thermal quenching evident in Fig. 2 was quantified by plotting $\ln[(I_u/I_q) - 1]$ against $1/kT_m$. The average activation energy of thermal quenching from three such measurements was determined as $\Delta E = 0.77 \pm 0.14$ eV.

4.3. Curve-fitting

In order to obtain additional kinetics data for comparison, the main peak was corrected for thermal quenching and analysed using curve-fitting on the basis of general order kinetics as described by Kitis [21]. The temperature dependence of the thermoluminescence

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