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On isothermal heating as a method of separating closely collocated thermoluminescence peaks for kinetic analysis

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ABSTRACT

The experimental separation of overlapping peaks is a common practical concern in thermoluminescence experiments. In this regard, we have investigated the use of isothermal heating as a method for separating closely collocated peaks for kinetic analysis. The method has been developed and applied on a sample of synthetic quartz in which the thermoluminescence intensity is not reproducible in successive measurements on the same aliquot. Preparatory experiments performed to establish a suitable combination of temperature and heating time are described in detail. A comparative analysis of results from conventional thermal cleaning with those from isothermal cleaning, done as a means to assess the effectiveness of the latter, has shown isothermal heating to be a reliable method of separating closely collocated glow-peaks. The method is conveniently applied in combination with a new technique for kinetic analysis based on the use of the temperature-dependence of the area under an isothermal decay-curve. Isothermal heating was also applied to separate collocated peaks in europium-doped orthosilicate ($Sr_2SiO_4:Eu^{2+}$), a luminophor, and in carbon-doped aluminium oxide (α-Al_2O_3:C), a dosemeter. The set studied in $Sr_2SiO_4:Eu^{2+}$, unlike in the quartz, consists of peaks where the intensity of the lower-temperature one is greater than subsequent ones at higher temperature. On the other hand, the example investigated in α-Al_2O_3:C is similar except that the dominant peak subsumes the lower intensity secondary peak to the extent that they appear as one.

1. Introduction

Thermoluminescence (TL) is a well-documented method of measuring low light levels from a previously irradiated semiconductor or insulator under a controlled heating rate [1]. The temperature-dependence of the emission appears as a set of peaks collectively termed as a glow-curve with each peak corresponding to an electron-trapping defect. TL glow-curves in some cases consist of well-defined peaks, and in others, of complex sets of overlapping ones as can be appreciated by a cursory examination of any of the many TL papers in the literature. Characteristic features of the peaks may be understood in terms of kinetic parameters, for example the activation energy, defining the electron traps. These parameters aid the description of the mechanisms involved in luminescence emission in the material concerned [1]. However, analysis of a peak for kinetic parameters can usually be conveniently done if the peak is isolated. As such, the experimental separation of overlapping TL peaks is a common practical problem and is the concern of this report.

The conventional method of separating overlapping peaks involves heating to just beyond the maximum of the first peak in order to deplete charge responsible for the 'satellite' thereby leaving the next peak with a clean rising edge. The main requirement in this so-called thermal cleaning method is that the partial heating should substantially remove charge responsible for the lower temperature peak. It seems to be reasonable then to expect that any other procedure that also selectively removes charge from a particular peak should affect thermal cleaning. In view of this, this report is concerned with static or isothermal rather than dynamic heating as a method of thermal cleaning.

Isothermal heating as a procedure for separating overlapping peaks was discussed by Pagonis and Shannon [2] who applied it on LiF:Mg,Ti. The method is based on the fact that when an irradiated sample is held at a constant temperature, some charge is lost from its electron traps. For this reason, isothermal heating should achieve the same purpose as the conventional thermal cleaning method. Pagonis and Shannon [2] observed the method to be of particular use in the case of first-order kinetics and added that it can be better exploited in combination with curve-fitting. One of the key requirements in the method of Pagonis and Shannon [2] is that the luminescence intensity from the same aliquot should be reproducible. To our knowledge, the technique has not been reported for materials in which this is not the case.

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This report is concerned with isothermal heating as a method of thermal cleaning and has been developed and applied on synthetic quartz in which the sensitivity changes due to the pre-dose effect. The quartz used here therefore exemplifies a material in which the TL intensity is not reproducible in successive measurements. Coincidentally, the glow-peaks on which the method was applied are closely collocated unlike in LiF (the test sample of Pagonis and Shannon [2]) where the peaks used are somewhat well separated. Preparatory experiments necessary before application of the isothermal cleaning method in this case have been described in detail. The effectiveness of the method was assessed by comparing kinetic parameters found from an isothermally cleaned peak with those determined from a peak thermally cleaned using the conventional thermal cleaning procedure. The method is most effective when used together with a new method of kinetic analysis [3] that uses the temperature-dependence of the area under an isothermal decay-curve.

We emphasize here that results from isothermal and conventional thermal cleaning methods were compared only to provide some evidence of reliability of the isothermal cleaning method to be discussed. The comparison must not be misinterpreted as an attempt to find which method is better.

The discussion is organized into three parts. The first one (Section 3.1) briefly presents results of kinetic analysis following conventional thermal cleaning. The second part (Section 3.2) describes experiments intended to establish a suitable combination of measurement temperature and heating time for use in isothermal heating. The third part (Section 3.3) then discusses results of kinetic analysis following isothermal heating. Taking advantage of phosphorescence emitted during isothermal cleaning, we applied (see Section 3.3.3) a new method of kinetic analysis [3] based on the temperature-dependence of the area under an isothermal decay curve.

The utility of the isothermal cleaning method is further demonstrated when the technique is applied to isolate TL peaks in europium-doped orthosilicate ($Sr_2SiO_4:Eu^{2+}$), a luminophor (Section 3.3.4) and to extract a collocate of the main peak in carbon-doped aluminium oxide (α-Al_2O_3:C), a dosemeter (Section 3.3.5). The set of peaks studied in $Sr_2SiO_4:Eu^{2+}$, unlike in the quartz, exemplifies a case where the intensity of the first peak at a lower temperature exceeds that of the neighbouring one at the higher temperature. On the other hand, the example studied in α-Al_2O_3:C is similar except that the dominant component subsumes the weaker-intensity one to the extent that the peaks appear as a single peak.

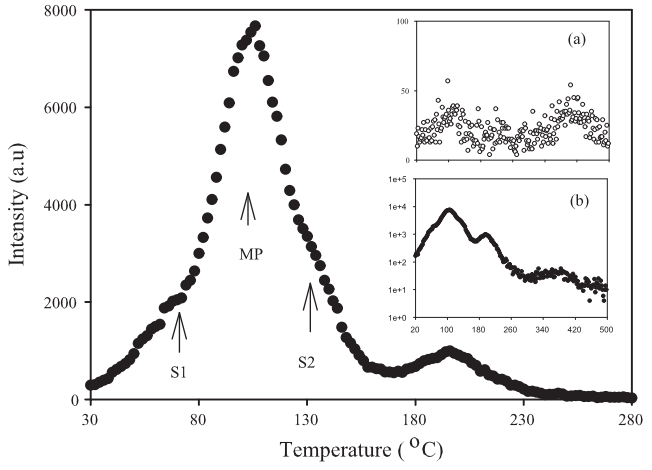

Fig. 1. A glow-curve measured from synthetic quartz at a heating rate of 5 °C s^{-1} following irradiation to 30 Gy. The insets show in (a) a glow-curve measured after irradiation but without any prior heating and in (b) the semi-logarithmic plot of intensity against temperature included to better show weaker intensity thermoluminescence peaks beyond 150 °C.

2. Experimental methods

The synthetic quartz used in this work was ground into coarse grains (90–500 μm) from a block supplied by Sawyer Research Products (OH, USA). 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 $^{90}Sr/^{90}Y$ beta source at a dose rate of 0.10 Gy s^{-1}. The thermoluminescence was measured in a nitrogen atmosphere to prevent spurious signals from air and to improve thermal contact between the sample holder and the heater planchet.

3. Results and discussion

The synthetic quartz used in this study produces negligible or no thermoluminescence if it is heated after irradiation only. Thermoluminescence is only properly observed after the sample has been preheated to a temperature above 300 °C before any irradiation.

Fig. 1 shows a glow-curve measured at 5 °C s^{-1} from a sample of synthetic quartz irradiated to 30 Gy. The glow-curve consists of at least 5 peaks (as clarified in the insets) at about 200 and 390 °C as well as the dominant peak near 100 °C which is overlapped at both ends by weaker intensity peaks at approximately 68 and 135 °C respectively. In illustrating the method of isothermal cleaning, this report discusses the kinetic analysis of the main peak and its lower-temperature 'satellite' in view of their location as part of the first three closely collocated peaks. The reason for choosing the two peaks studied will be explained later in the text. To aid visual clarity, the glow-curve otherwise measured to 500 °C is shown truncated at 280 °C in Fig. 1. For ease of reference, the main peak is labelled MP and its 'satellites' denoted S1 and S2.

In this section and elsewhere in the text, collocation refers to the case where a significant component or all of a peak is concealed by another with which it overlaps. Examples of collocated peaks include high-temperature secondary peaks in γ-irradiated α-Al_2O_3:C [4], TL emission near 700 nm in Mn or Cr doped beryl [5], TL in X-ray irradiated CaF_2:Dy [6] and many others in the literature. The main peak in α-Al_2O_3:C is a topical example and will be discussed in Section 3.3.5.

3.1. Kinetic analysis using the conventional thermal cleaning method

In these series of experiments, the main peak was cleaned of its lower temperature overlapping 'satellite' by applying the conventional thermal cleaning method described by McKeever [1]. Wherever necessary, a sample irradiated to 30 Gy was heated to 70 °C at 5 °C s^{-1} in order to remove peak S1 after which the complete glow-curve was measured by heating to 500 °C at the same rate. It should be emphasized that the only necessary and sufficient condition for using the thermal cleaning method is that the sample ought to be heated to a temperature just beyond the maximum of the peak immediately before the one to be analysed.

Kinetic parameters associated with the main peak were determined, after conventional thermal cleaning using the initial-rise and various heating rate methods discussed elsewhere [1]. The values found are subsequently compared with those evaluated after an alternative thermal cleaning method, isothermal heating, to be described later.