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Time-resolved OSL of natural zircon: A preliminary study

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HIGHLIGHTS

- Time-Resolved OSL from natural zircon was studied.
- Two components with lifetimes 17 and 110 us were observed.
- TR-OSL signal is found to be stable up to 250 °C.
- Dose Response of the TR-OSL signal was found to be linear over a dose range of 1–1000 Gy.
- Thermal quenching energies of the two components were found as 0.18 and 0.24 eV.

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ABSTRACT

Time-resolved OSL (TR-OSL) from natural zircon ($ZrSiO_4$) minerals was investigated using 445 nm blue laser light for stimulation. Analyses of the TR-OSL spectra have showed that the decay is composed of two exponential components with lifetimes varying around ~17 μs and around ~110 μs respectively. The behaviour of these signal components, was examined under various sample treatments and experimental conditions. Preheating experiments showed that the OSL signal is stable up to temperatures ~250 °C then becomes unstable. The dose response of the TR-OSL signal from zircon was determined in the range from 1 Gy to 1 kGy and observed to be increasing linearly. Practically, no effect of radiation dose on the lifetimes of signal components was observed. In addition, the effect of measurement temperature on the TR-OSL decay lifetimes was also investigated. Thermal quenching energies of the "*fast*" and the "*slow*" components were found to be very close to each other i.e. 0.18 and 0.24 eV respectively.

1. Introduction

Optically Stimulated Luminescence (OSL) is the emission of light from a previously irradiated solid (a wide band gap semiconductor or an insulator), upon stimulation with photons. Irradiation with ionizing radiation creates free electrons and holes where a portion of them have probability of being captured by defect centres which act as trapping states. If these states are deep enough (to prevent the thermal escape of the trapped charges), trapped charges accumulate in a manner that the number of trapped charges is a measure of radiation dose absorbed by the sample. Upon stimulation with light of appropriate energy, trapped electrons are delocalized and subsequently have a chance to recombine with the holes. If this recombination is radiative, a weak luminescence is emitted. The intensity of the emitted light is dependent on the radiation dose and this dependence allows the development of a radiation dosimetry system when luminescence intensity is calibrated against the radiation dose. The technique is widely used in various fields of radiation dosimetry and also for age determination of archaeological and geological findings. Comprehensive reviews of the technique and its applications can be found in books by Bøtter-Jensen et al. (2003) and Yukihara and McKeever (2011).

Conventionally, OSL is measured using a simple technique called Continuous-Wave OSL (CW-OSL) where the time development of the luminescence is recorded after turning on the stimulation light and keeping it constant for the duration of the experiment. Such a measurement, in general, results in a monotonic decay of luminescence; and the rate of the decay is mainly dependent on the photo-ionization cross-section of the electron traps and the stimulation light intensity (assuming a monochromatic stimulation light). Thus a CW-OSL measurement mainly characterizes the electron trapping centers. A modification of the CW-OSL technique is the Linearly Modulated-OSL (LM-OSL) which is based on the linear increase of the stimulation light intensity during the measurement (Bulur, 1996) which results in peak shaped OSL curves rather than the exponential-like decay curves of CW-OSL. A different way of measuring the OSL signals is to use short pulses of stimulation light and detection of OSL

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signal generally after the end of the stimulation pulse. Such a measurement scheme is called pulsed OSL and has been applied to record OSL from Al_2O_3:C (see e.g. McKeever et al., 1996; Bulur and Göksu, 1997). In pulsed OSL measurements, generally, the main motivation is the measurement of the absorbed radiation dose; thus the integrated intensity of the emission following the end of the stimulation pulse is recorded. Time-Resolved Optically Stimulated Luminescence (TR-OSL) is a pulsed OSL technique which takes into account the time development of the luminescence signal both during and following a short pulse of stimulation light (see e.g. Chithambo, 2007a,b). The time intervals considered are very short -compared to the CW-OSL case- and from TR-OSL one obtains information about the recombination part of the OSL production mechanisms. Generally, the decay part of the signal (measured after the end of the stimulation) is utilized to determine the characteristic decay lifetime of the luminescence emission. In most of the cases, where one type of recombination centre is considered, the luminescence decay after turning off the light pulse can be written as

$$L(t) = L_0 \exp\left(-\frac{t}{\tau}\right) + B. \quad (1)$$

Here L_0 and B are constants representing the initial signal intensity and the background signals respectively and τ is the lifetime of the luminescence decay. In most cases, the luminescence signal intensity obtained by a single pulse is very weak (in some cases a few photons per pulse), and because of this the luminescence needs to be accumulated over a number of pulses to attain a reasonably high signal to noise ratio.

The TR-OSL decay curve supply information about the luminescence emission processes. The lifetime τ is determined by the radiative relaxation probability from an excited state to the ground state of the recombination centre. The decay lifetime is dependent on the quantum mechanical transition probabilities. Thus, the study of the TR-OSL combined with emission spectroscopy can be helpful in characterizing and identifying the luminescence emission centres. Although time-resolved luminescence (TRL) techniques relevant to naturally occurring minerals have been in use for a long time (see e.g. Gaft et al., 2005), TR-OSL is a relatively new technique and has been applied to feldspars; quartz, alumina, BeO and other materials (see e.g. Bøtter-Jensen et al., 2003; Yukihara and McKeever, 2011 for a recent review).

Zircon ($ZrSiO_4$) is an abundant mineral in the earth's crust and has been considered as a suitable material for absolute age determination using TL by several investigators (see e.g. Zimmerman et al., 1974; Sutton and Zimmerman, 1976; Aitken, 1985; Templer, 1986; Smith, 1988; van Es et al., 2000, 2002a, b; Turkin et al., 2003, 2005) because of its occurrence in sand-rich sedimentary deposits, high chemical stability and high internal dose rate due to substitution of U and Th in the crystal lattice. High content of U and Th, results in a high internal dose rate which irradiate the material internally at dose rates much higher than the dose rate from external environmental sources. This makes zircon a favourable material for age determination using luminescence, essentially for dating of young samples. Auto-regenerative techniques for luminescence dating using zircon inclusions have been suggested and the high internal dose rate in zircon allows a measurable auto-regenerated TL signal after a few months (e.g. Templer, 1986; Smith et al., 1986; Smith, 1988; Templer and Smith, 1988). Reports on the systematic studies of the OSL from zircon are not as common as TL studies. Initial systematic studies on the OSL properties of the material go back to mid nineteen eighties: OSL properties of $ZrSiO_4$ were first mentioned by Smith et al. (1986), Smith (1988), and Godfrey-Smith et al. (1989) which were then followed by Turkin et al. (2006, 2007), Secu et al. (2007).

To our knowledge no TR-OSL experiments on $ZrSiO_4$ mineral have been reported so far. In a recent book, Gaft et al. (2005) summarized time resolved luminescence (TRL) studies measured using pulsed laser excitation. They reported that using pulsed laser excitation it was possible to identify emission centers related to radiation induced defects and trivalent rare earth elements (such as Gd^{3+}, Ce^{3+}, Tb^{3+}, Tm^{3+}, Er^{3+}, Ho^{3+}, Dy^{3+}, Eu^{3+}, Sm^{3+}, Yb^{3+} and Nd^{3+}) and also $(UO_2)^{2+}$; Fe^{3+} and Cr^{3+}. However, these measurements were related to prompt photoluminescence (PL) emission in a time resolved manner. In this paper, TR-OSL spectra from heated natural zircon mineral and its behaviour under various experimental conditions and sample pre-treatments are presented.

2. Materials and methods

Gem quality brown zircon crystals (from Cambodia) were used for the experiments. Before the experiments samples were heated at 900 °C for about 15 min. Heating the samples removed the colour of the beads; totally transparent or light orange colour beads were obtained. Heated zircon beads of average size ~6 mm were crushed and ground in an agate mortar to a size of ~100 microns. Powders were mixed to obtain a homogeneous sample. All the measurements were carried out using aliquots of this homogenised mixture. For OSL measurements, a single layer of grains were fixed to aluminium disks of diameter 10 mm using silicone oil. Irradiations were done using a $^{90}Sr/^{90}Y$ beta source (approximate dose rate is ~30 mGy/s).

TR-OSL measurements were performed using a home-made setup based on a blue laser module emitting at 445 nm for stimulation. All measurements were carried out using a filter combination (Hoya U340 and Schott DUG 11) transmitting in the 280–380 nm region of the electromagnetic spectrum. Luminescence is detected using a PMT with a bialkali photocathode (Hamamatsu R268P). Pulses from the PM tube were counted using a multichannel scaler/averager (Stanford Research Systems, SR430) which can record the time resolved evolution of luminescence pulses by scaling the time of arrival of pulses coming from the PMT. The basic structure of the setup and the operating principles were mentioned in a recent paper by Bulur and Saraç (2013). If otherwise not noted, TR-OSL of irradiated zircon samples were measured after preheating (to delete the luminescence signals originating from shallow traps) at 150 °C for 15 min using 100 μs stimulation pulses and 0.32 μs bin-widths at room temperature.

CW-OSL decay curves and TL glow curves were measured using an automated TL-OSL reader (Risø National Laboratory, Denmark) which is equipped with blue LEDs (λ_p ~ 470 nm) and a bialkali photomultiplier tube (ET Enterprises Ltd. 9235QA) with a Hoya U-340 filter in front.

3. Results and discussions

3.1. TR-OSL signal

A representative example of a TR-OSL signal from zircon is given in Fig. 1. TR-OSL decay curve was measured, using a 50 Gy irradiated sample after preheating (to delete the luminescence signals originating from shallow traps) the sample at 150 °C for 15 min. Data were collected using 100 μs stimulation and 0.32 μs bin-widths with 10^5 accumulations. TR-OSL spectra of zircon can be approximated successfully by a double exponential decay function of the form

$$L(t) = L_{01}e^{-t/\tau_1/} + L_{02}e^{-t/\tau_2} + b \quad (2)$$

where L_{01}, L_{02} are the amplitudes and τ_1, τ_2 are the lifetimes of each component and b is the background signal. As a result of analysis by curve fitting, the component lifetimes were determined as 13 μs