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Studies of excitation, optical bleaching and thermal annealing of OSL in natural quartz

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Abstract. Optically stimulated luminescence (OSL) was excited at LNT by monochromatic light in x-irradiated natural quartz crystals. Excitation maxima appeared at 290 and 310 nm. The phototransferred thermoluminescence (PTTL) of these crystals showed excitation maxima at the same wavelengths, indicating that carriers are optically stimulated from the same traps. This is supported by the finding that the same wavelengths are most efficient for optical bleaching caused by prolonged illumination. The effects of thermal annealing to gradually increasing temperatures on the OSL were investigated and a correlation to thermoluminescence (TL) peaks was found. The OSL intensities showed sharp decreases after annealing to 160, 190 and 280 K; these temperatures coincide with the temperatures of the main TL glow peaks. It appears therefore that the OSL and the main TL peaks between liquid nitrogen temperature (LNT) and room temperature (RT) are due to the same donor levels. The emission spectrum of the OSL showed that this emission is composed of some bands, which appear also in PTTL as well as in x- and photoluminescence, indicating that the same luminescence centres are responsible for these emissions.

1. Introduction

Optically stimulated luminescence (OSL) and its application to dosimetry and dating have previously been suggested by some authors [1, 2]. During recent years this method has frequently been used for the dating of various geological and archaeological materials [e.g. 3, 4]. In this method, samples which have previously been exposed to ionizing radiation are illuminated by light of photoenergies which cannot directly excite luminescence in unirradiated samples. These low-energy photons can, however, stimulate carriers, which were trapped following ionizing radiation. Recombination of the optically stimulated carriers with carriers of opposite sign may result in the emission of OSL. In this respect OSL is similar to phototransferred thermoluminescence (PTTL). The processes of PTTL have been described by many authors [e.g. 5]. Both OSL and PTTL can be excited only in crystals which have previously been exposed to ionizing radiation. The optical stimulation of trapped carriers may result in the emission of OSL or in the transfer of the stimulated carriers from deep to shallower traps, which are stable at low temperature only. PTTL is emitted if, during heating, trapped carriers are thermally released and recombine with carriers of opposite sign at luminescence centres.

In a recent study, OSL excited at RT in synthetic quartz has been investigated [6]. In the present work these studies are extended to lower temperatures and to natural quartz crystals. In most previous work OSL was initiated by the powerful radiation of an argon laser at 514.5 nm. For most of our present investigations luminescence was excited by monochromatic light in a broad spectral range and stimulation spectra were measured. For comparison, the low-temperature PTTL and TL of the samples were measured; the effects of optical and thermal bleaching were also studied. In this respect, some recent work on OSL, PTTL and on bleaching effects should be mentioned — the works of McKeever [7], McKeever and Morris [8] and Fain *et al* [9]. McKeever [7] explains the bleaching as being mainly associated with the loss of recombination centres rather than with the emptying of traps. The light is assumed to empty electrons from deep, thermally disconnected centres only; the freed electrons can then recombine with the trapped holes, thus reducing the number available for TL, and a similar model is given for PTTL results. The effects occurring in OSL and PTTL are numerically simulated from the model by McKeever and Morris [8]. Fain *et al* [9] utilize a similar model with a large disconnected trapping state for explaining dose dependence and sensitization of TL. These authors further use the notion of partial correlation between TL traps and hole centres for explaining some of the above mentioned experimental results. Finally, some experimental results of bleaching of TL in quartz have been reported by Morris and McKeever

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[10]. However, comparison of these results with those given here is difficult due to the differences between the natural, Arkansas quartz used by these investigators and the quartz samples used in the present work.

2. Experimental procedure

For our measurements natural Norwegian quartz crystals from British Drug House (BDH) were used. For the low-temperature measurements the samples were kept in a liquid nitrogen cryostat, equipped with three fused silica windows for the illuminations and the optical measurements and one aluminium window for the x-irradiations. The fused silica windows, used in the present work, were transparent from about 1200 to 180 nm. The temperature was measured with a copper–constantan thermocouple. The β-irradiations were performed with Sr^{90} beta source. The samples were normally exposed to doses in the range 5–10 Gy. For the x-irradiations a tungsten tube (40 kV, 15 mA) was used. For the monochromatic illuminations, a 150 W high-pressure Xe lamp and a 0.25 m grating double monochromator were used. The reciprocal linear dispersion of the analysing monochromator was 3.3 nm mm^{-1}, the slit width was normally 1 mm. The irradiance of the incident light beam was measured with Molectron pyroelectric radiometer. The emission spectra were measured with a 0.5 m Bausch and Lomb grating monochromator, equipped with a fast scanning stepping motor and were recorded with an EMI 9789Q photomultiplier. The TL measurements were taken during heating from LNT to RT at a constant rate of 20 °C min^{-1}. Further experimental details have been given elsewhere [11].

3. Experimental results

OSL was initiated at LNT by monochromatic light in the spectral region 270 to 350 nm in natural quartz crystals which had previously been irradiated with β- or x-rays. The stimulation spectrum of the OSL emission showed a main maximum at 290 nm and a weaker one at 310 nm (curve a of figure 1). Our previous measurements of synthetic quartz at RT showed a strong stimulation maximum at 330 nm (see figure 2 of reference [6]). By wavelengths shorter than 270 nm a photoluminescence (PL) emission could be excited at LNT in natural quartz crystals; however, PL emission could also be excited in samples which had previously not been exposed to ionizing radiation. The PL showed (at LNT) a strong emission band at about 440 nm with an excitation maximum at 250 nm (curve b of figure 1). These results fit previous observations on PL in natural quartz [12]. The 440 nm emission band is also the main emission band of the luminescence emitted during x-irradiation (XL) at LNT. In figure 2 the emission spectra of OSL, PL and XL at LNT are shown by curves a, b and c respectively. The emission spectrum of the relatively low-intensity OSL showed a broad, apparently composed, band between 350 nm and 500 nm.

In the present work OSL was also compared to PTTL in the same crystals. Crystals which had previously been exposed to x or β irradiation at RT and were subsequently illuminated at LNT with monochromatic UV light in the same spectral region between 270 and 350 nm showed a main glow peak at about 190 K and weaker ones at 160 and 230 K (figure 3) during heating. No glow curves could be excited with UV light in the 270–340 nm spectral region in crystals which had not previously been exposed to ionizing radiation. This thermally stimulated emission is therefore attributed to a process of PTTL. The emission spectra of the PTTL peaks between 80 K and about 300 K showed a main emission band near 400 nm (figure 2, curve d). Excitation spectra of PTTL were measured for comparison and results are given in curve c of figure 1. It can be seen that the excitation maxima of PTTL at 290 nm and 310 nm coincide with the excitation maxima of the OSL in the same samples. Crystals which were x-irradiated at LNT without any subsequent UV illumination showed, during heating from 80 to 400 K, several TL glow peaks, the main one being at 160 K (curve a of figure 4).

Special attention was given to the study of optical and

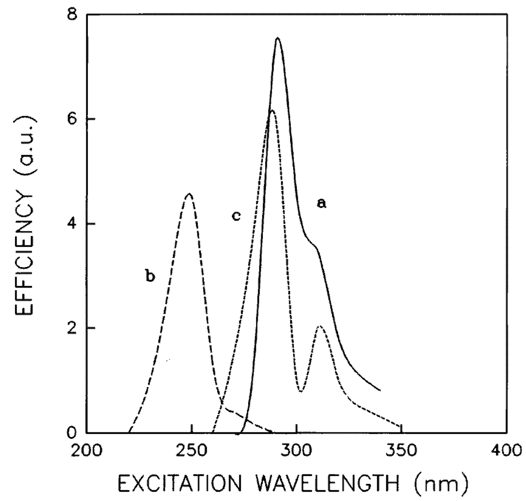

Figure 1. Excitation spectra of: a, OSL; b, PL; c, PTTL of natural quartz at LNT.

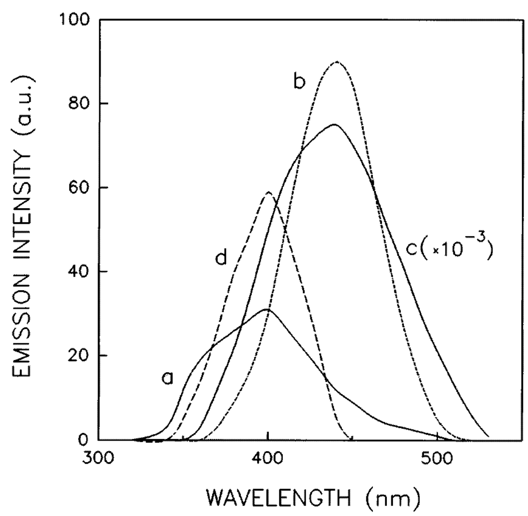

Figure 2. Emission spectra of: a, OSL; b, PL; c, XL at 80 K and d, of 190 K PTTL peak.

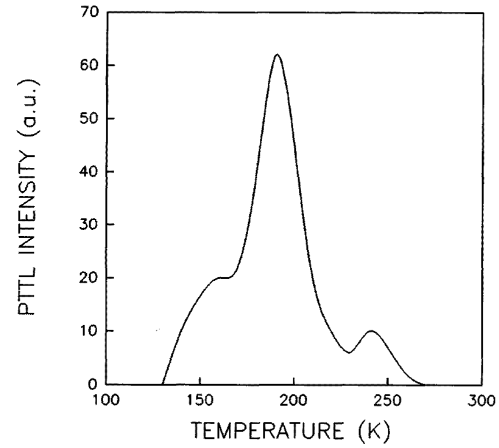

Figure 3. PTTL of an x-irradiated crystal, stimulated by 310 nm light at 80 K.

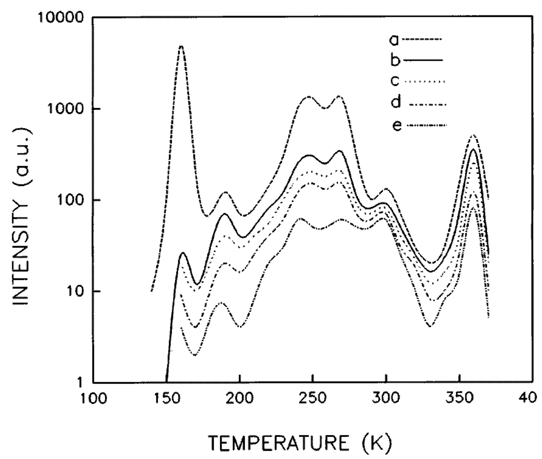

Figure 4. Effects of illumination on TL: a, after x-irradiation at LNT; b, c, d, e, after subsequent 2, 5, 30, 90 min illumination with polychromatic light from Xe lamp (zero order of monochromator) respectively.

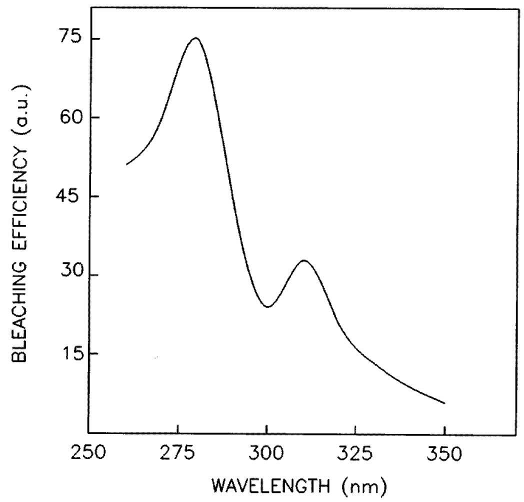

Figure 5. Relative efficiency of the optical bleaching of PTTL as a function of illumination wavelength.

thermal bleaching of TL, PTTL and OSL. Results showed that prolonged illumination at LNT with polychromatic as well as with monochromatic light of appropriate wavelengths had a notable influence on PTTL and TL as well as on OSL intensities. Curves b, c, d and e in figure 4 show the TL recorded in the natural quartz crystals which were x-irradiated at LNT and subsequently exposed to polychromatic (zero order of monochromator) light from a Xe lamp for 2, 5, 30 and 90 min respectively. Comparison with curve a of figure 4 shows a notable decrease in TL intensities with increasing duration of illumination.

The wavelength dependence of the efficiency of optical bleaching was also investigated. UV light in the spectral region 280–350 nm was found to be most efficient for optical bleaching of most of the PTTL and TL peaks (figure 5). In figure 5 the bleaching efficiency of the main PTTL is given as function of illumination wavelength. The same wavelengths were most efficient for the main TL peak. The 160 K could also be optically bleached by longer wavelengths even by visible light up to 500 nm. The prolonged illumination with polychromatic light of the x-irradiated samples also caused a decrease in OSL intensities. The intensities of the monochromatic light obtained by our light sources and monochromator were, however, too low to measure bleaching effects on OSL. Measurements with optical filters showed that UV light in the same spectral region which is most efficient for bleaching PTTL and TL is also most efficient for bleaching OSL. However, OSL intensities increased again after additional exposure to x-rays.

Effects of heating to various temperatures on the OSL emission were also investigated. After the first measurement of OSL at LNT the samples were heated step by step to gradually increasing temperatures and kept at these temperatures for about 5 min. After each step the crystal was recooled and OSL was again measured at LNT. In curve a of figure 6 the OSL intensities, measured at LNT after each heating step, are given as a function of annealing temperature. The results show that the heating caused a notable decrease in OSL intensities at certain temperatures. For comparison, the TL of the same sample is given by curve b of figure 6. It can be seen that the main decreases in OSL occur near 160, 190 and 280 K. These temperatures correspond to the temperatures of the main TL glow peaks.

4. Discussion

Our experimental results have shown that the excitation spectrum of OSL of quartz crystals, which had previously been exposed to an ionizing radiation, has maxima at 290 and 310 nm. OSL cannot be excited by these wavelengths in unirradiated quartz crystals. Results also showed that PTTL of the crystals has excitation maxima at the same wavelengths. It should, however be noted that for the OSL measurements, UV illumination as well as x-irradiation was performed at LNT, while for the PTTL measurements only UV illumination was at LNT, while x-irradiation was carried out at RT. The finding that OSL and PTTL have excitation maxima at the same wavelengths of 290 nm and 310 nm indicates that despite the differences in irradiation

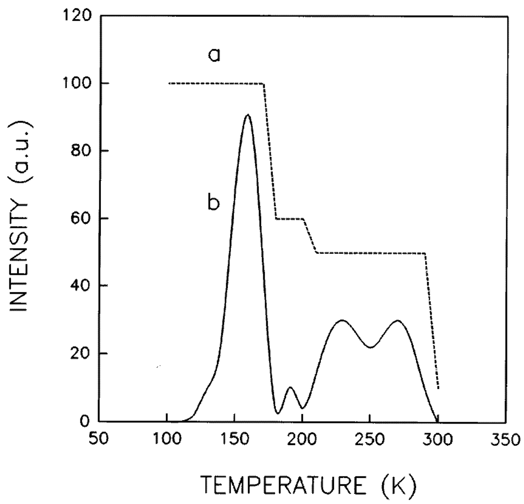

Figure 6. Curve a, OSL intensities of x-irradiated crystal after a step by step heating from 80 to 300 K; curve b, TL induced by x-irradiation at 80 K.

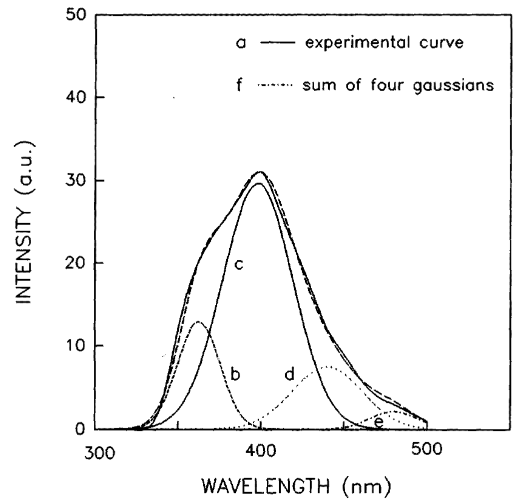

Figure 7. OSL emission. Experimental curve at 80 K (curve a), numerically resolved into four Gaussians, centred at: b, 360 nm; c, 400 nm; d, 440 nm; e, 480 nm; f, sum of curves b, c, d and e.

temperatures, carriers are stimulated in both cases from the same traps. At RT, only deeper traps are stable, but cooling to LNT and UV illumination at this temperature may cause the transfer of carriers from deep to shallow traps or their optical stimulation and radiative recombination with carriers of opposite sign, resulting in the emission of OSL. The carriers trapped at the shallow traps are thermally released during heating from LNT to RT and their radiative recombination at luminescence centres may result in a PTTL emission.

Experimental results have shown that wavelengths of 290 and 310 nm are most efficient for optical bleaching (see figure 5). These wavelengths coincide with the maxima of the excitation spectrum. The finding that UV light of the same wavelength is also most effective for optical bleaching of PTTL, TL and OSL supports the conclusion that they are due to the same traps. Prolonged illumination at these wavelengths apparently causes depletion of the traps, resulting in the observed optical bleaching. The wavelength of 290 nm corresponds to an electron trapping level of 4.3 eV below the conduction band. A level of this photoenergy was previously attributed to Ge impurities present in natural quartz [13].

The observation that the OSL intensities strongly decrease after thermal annealing to temperatures which correspond to the main TL peaks also supports the conclusion that the OSL and TL peaks between LNT and RT are due to the same donor levels.

The broad emission band observed in OSL between 350 and 500 nm appears to be an envelope covering several emission bands. The broad OSL emission band given by curve a of figure 2 has been resolved numerically into four bands of Gaussian shape centred at 360, 400, 440 and 480 nm, shown by curves b, c, d and e of figure 7. Curve a of this figure shows the experimental curve (enlarged curve a of figure 2) and curve f shows the sum of the four Gaussians. The main component of the OSL emission at 400 nm is also the main emission band of PTTL in the temperature range between 80 and 300 K, indicating that these OSL and PTTL emissions are due to the same luminescence centres. On the other hand the main PL and XL emission bands at LNT (curves b and c of figure 2) were recorded at 440 nm; OSL apparently also has a component at this wavelength. The emission band near 440 nm has previously been attributed to an intrinsic STE emission [11, 14, 15]. The component of the OSL emission near 360 nm has previously been ascribed to the recombination of electrons with holes trapped at Al^{+3}–M^{+} centres.

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