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Effects of photostimulation in natural zircon

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Abstract

Effects of optical stimulation were studied in unirradiated as well as in X, β and VUV irradiated natural zircon crystals. Various optical and dosimetric properties were investigated and in particular thermoluminescence (TL) and optically stimulated thermoluminescence (OSTL or PTTL), as well as optically stimulated luminescence (OSL). After X or β irradiation at RT, main TL peaks appeared in the samples at about 354, 385 K and weaker ones at about 470, 520 and near 600 K. TL could also be excited by monochromatic VUV radiation. Results show that the same traps are responsible for the TL induced by VUV as by X or β irradiation. In pre-irradiated samples, a notable OSTL was recorded below RT as well as at about 420 K. The same emission bands appeared in the XL as in various TL and OSTL peaks, indicating the same luminescence centers are involved in these emissions. OSTL stimulation spectra showed maxima at 425 and 294 nm. Prolonged illumination with these wavelengths also caused a notable decrease in the OSTL; this bleaching effect is attributed to the depletion of the carriers from the trap responsible for the phototransfer. The TL sensitivity of the main TL peaks below 400 K was $\sim \frac{1}{10}$ of that of TLD-100, and that of the higher temperature TL peaks was even lower by 1–2 orders of magnitude. The TL peaks below 400 K are subject to fast thermal fading at RT. The application of the OSTL method may therefore be preferable to the regular TL method in these crystals.

Keywords: Luminescence; Radiation effects; Photostimulation; Dosimetry; Zircon

1. Introduction

Due to the internal radioactivity of impurities like uranium, natural zircon ($ZrSiO_4$) has some advantages for application in TL dating over the commonly used quartz and has therefore been used by some investigators in dating of sediments (e.g. Templer, 1985, 1986). Radiation effects, as well as photoluminescence (PL), X-luminescence (XL) and thermoluminescence (TL) in zircon have previously been studied by various authors (e.g. van Es et al., 2002; Spetsius et al., 2002). Some main TL peaks in zircon fade, however, very rapidly close to the ambient temperature, due to recombination of trapped carriers with carriers of the opposite sign; the fading properties of a zircon sample have therefore to be carefully investigated, when considering it for TL dating. Methods of optically stimulated thermoluminescence (OSTL), have some advantages over regular TL. The phenomenon of OSTL was first reported by Stoddard (1960) in NaCl and was later observed in various other insulating materials. In this process a sample is exposed at a given temperature T_1 such as room temperature (RT) to ionizing radiation and then cooled to a lower temperature T_2 such as that of liquid nitrogen (LNT) and illuminated with monochromatic light of wavelengths that normally cannot excite any TL in this material. During subsequent heating to RT, various glow peaks may appear between LNT and RT, although no TL emission is expected below the temperature of ionizing irradiation without the additional stimulating light exposure. The appearance of OSTL glow-peaks in the range between the temperature of illumination (LNT) and that of exposure to ionizing radiation (RT) is attributed to a process of optical stimulation. The efficiency of this process was found to depend on the wavelength of the illuminating light (e.g. in alkali halides, illumination in the F-absorption band was most efficient for stimulation of these glow-peaks). The application of OSTL to dosimetry and dating has also been investigated by some authors (e.g. Bailiff et al., 1977; Oster et al., 1994). In the context of

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dosimetry and dating, OSTL is also called phototransferred TL (PTTL). The OSTL method has various advantages for dosimetry over the common TL method, such as: (1) short exposures to light cause only a relatively slight depletion of the carriers that were trapped at the deep traps by the original ionizing radiation. This fact enables repeated exposures to radiation. (2) The OSTL measurements can be carried out at relatively low temperatures even for evaluation of concentrations of carriers in deep traps. In the common TL measurements, a specimen has to be heated to high temperatures in order to release carriers thermally from such deep traps, in which case the TL emission may be overlapped by blackbody radiation. (3) Fading effects, which are typical of low-temperature TL peaks, may be avoided by application of the OSTL method, since in the latter method relatively deep traps are used for the measurements. This is of importance for various applications in which specimens are kept for very long periods of time between the exposure to radiation and the readout. OSTL is therefore of special interest for application to dating. Solid state dosimeters (SSD) are sometimes also based on the effect of optically stimulated luminescence (OSL) (e.g. Wintle, 1993). The OSL, like the OSTL, appears only in solids, which have previously been exposed, to ionizing radiation. Most of the previous studies on radiation effects and the formation of point defects in these crystals concentrated on the effects of higher energy radiations such as β, γ and X-rays, and relatively few works dealt with the effects induced by monochromatic VUV radiation (e.g. Lushchik et al., 2002; Kristianpoller et al., 2005). This is mainly due to the relatively low intensities of the light sources, which makes it difficult to detect and to measure low concentrations of the defects. It has previously been shown that in some broadband crystals, the application of monochromatic VUV radiation can be very useful for studying processes of defect formation since it also enables the measurements of the spectral dependence of the production efficiency of the radiation-induced defects.

In the present work, the effects of X, β and UV irradiations were studied in natural zircon crystals. The XL, PL, TL, OSTL and OSL as well as optical absorption and effects of optical bleaching were investigated. The dependence of the TL and OSTL on the radiation dose was also investigated and the luminescence efficiency of the material was compared to that of other known dosimetric materials.

2. Experimental techniques

The zircon specimens used in this work were from Yakutia, Russia. These crystals are known to have distinctive traces of radioactive elements, such as uranium and concentrations of 10–1000 p.p.m. are typical of natural zircon crystals (Templer, 1985, 1986; Spetsius et al., 2002). The samples used here were "as received" and not selected; they looked colorless. The X-irradiations were performed with a W-tube (40 kV, 15 mA), the β irradiations with a ^{90}Sr source (dose rate: 1.5 Gy/min) and the VUV irradiations with a 1-m normal-incident VUV monochromator and an H_2 arc lamp. The TL and OSTL measurements above RT were carried out in a TL compartment flushed by N_2 gas; the heating rate above RT was 5 K/s. For the low temperature measurements, the samples were kept in a liquid nitrogen vacuum cryostat and heated at a rate of 20 K/min. For the OSL measurements, the crystal was stimulated at various temperatures between 80 and 400 K by monochromatic UV and visible light in samples, which had previously been exposed to X, or β radiation. The optical absorption in the visible and near UV was measured with a Cary 17 spectrophotometer and in the VUV region with the VUV monochromator. The PL, OSL, TL and OSTL measurements were taken with an Aminco-Bowman/2 luminescence-spectrometer. Optical bleaching of radiation-induced defects was realized using a 175 W Xe Illuminator (ICL Technology, Inc., #LX175uv) or a 150 W halogen lamp and a grating monochromator. Further experimental details are given elsewhere (Kristianpoller et al., 2001).

3. Results and discussion

TL glow peaks appeared during first heating without exposure to any radiation at the laboratory; TL peaks were recorded at about 400 and 425 K and somewhat stronger ones near 520 and 640 K; these peaks are attributed to internal radioactive impurities in the zircon samples. After re-cooling of the sample and X, β or far UV irradiation, a stronger TL emission was recorded. After X irradiation at LNT, the main TL glow peaks appeared below RT at about 158, 180, 265 K (Fig. 1). After X or β irradiation at RT relatively strong TL glow peaks were

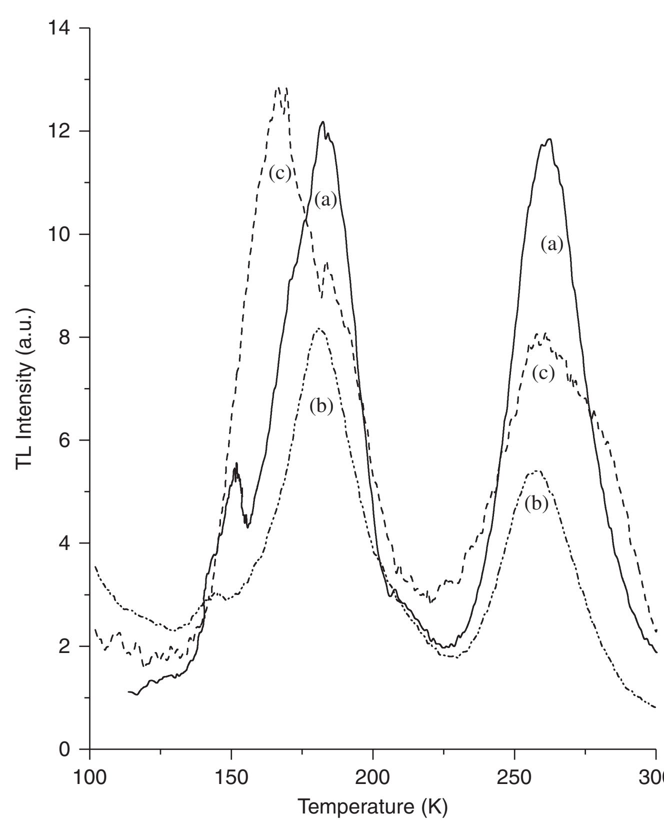

Fig. 1. TL induced at LNT by: (a) X-rays, (b) 190 nm, and (c) 161 nm; the heating rate was 20 K/min.

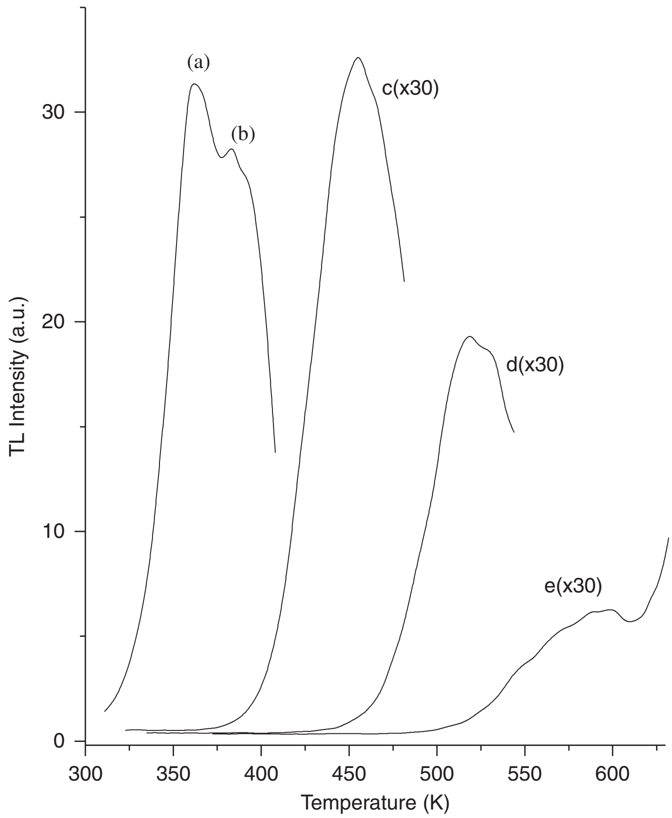

Fig. 2. TL after β irradiation at RT, recorded during gradual (four-step) heating.

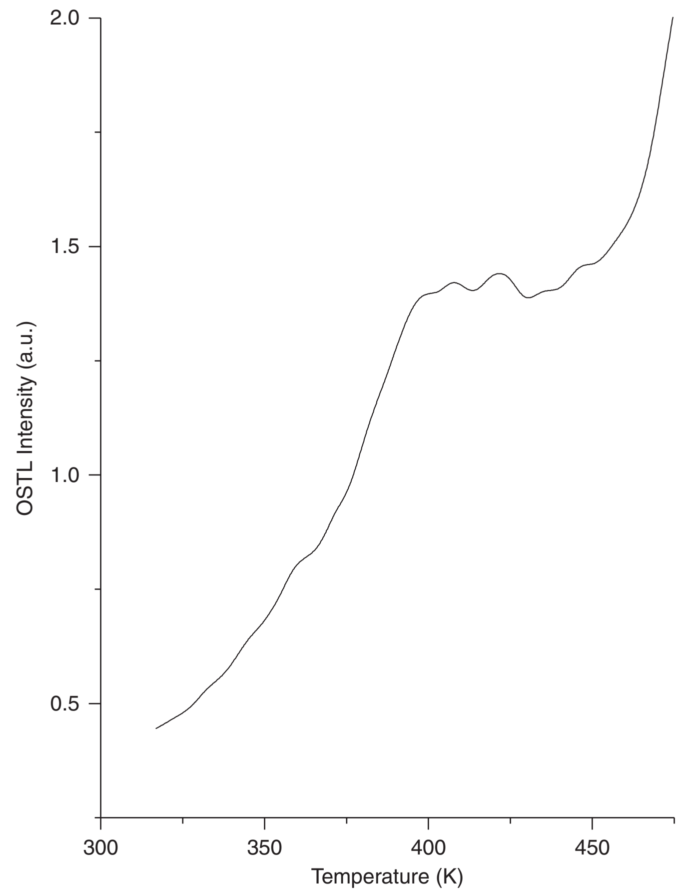

Fig. 3. OSTL of zircon, after β irradiation at RT (180 Gy), subsequent TL recording during heating to 460 K, re-cooling to RT and illumination with 425 nm light at RT.

recorded at 354 and 385 K and much weaker ones at 470, 520 and near 600 K. Since the higher temperature peaks were much weaker, they were resolved by a method of gradual step-by-step heating. A sample of TL curves, recorded during gradual heating, is given in Fig. 2. The crystal was β-irradiated at RT and TL was first recorded during heating from RT to above the first strong low temperature peaks (to $\sim$ 440 K); the sample was then re-cooled to RT and the weaker peaks at higher temperature were recorded in additional heating cycles, by setting the detection system to higher sensitivities. Essentially the same main glow peaks also appeared after VUV as after X or β irradiation, indicating that the same traps are responsible for the TL induced by the different types of radiation. The far UV excitation spectra showed main maxima in the VUV at 140 and 190 nm, and some very weak maxima at the long wavelength tail of the fundamental absorption between 200 and about 250 nm. Absorption spectra and thermal stability of radiation-induced bands were also investigated. The optical density of the non-irradiated samples showed a steep increase below 230 nm, resembling the onset of the fundamental absorption and in the VUV region additional absorption peaks were recorded near 190, 175, 150 and 140 nm. After prolonged β- or X-irradiation at RT, additional absorption bands appeared at 430 and 255 nm, these two bands were annealed by heating to $\sim$ 800 K. Samples that had previously been exposed to ionizing radiation and were not thermally annealed showed also a notable OSTL, but no measurable OSL emission could be detected when stimulated with monochromatic visible or near UV light, even by application of high β doses and illumination light beams. For measurements of OSTL, the zircon sample was exposed at RT to ionizing X or β radiation and then either cooled to LNT and illuminated at LNT with light of wavelengths that normally cannot excite any TL in this material. In another version of OSTL, the sample is heated from RT to above the first strong TL peaks (to $\sim$ 460 K), re-cooled and illuminated at RT with light of appropriate wavelength that normally cannot excite any TL in this material. In the first case glow peaks appeared between LNT and RT and in the second case between RT and the temperature of the thermal annealing (460 K) although no TL emission is expected in this temperature region without the stimulation. These glow peaks are attributed in both cases to a process of optical stimulation (OSTL), whereby carriers are trapped by the ionizing irradiation in relatively deep traps and then stimulated at lower temperatures by non-ionizing light of appropriate wavelength and transferred to shallower traps, which are not stable at the temperature of ionizing irradiation. OSTL glow peaks appear during re-heating, when carriers are thermally released from the shallow traps and recombine radiatively with carriers of opposite sign. The main OSTL peaks appeared in the first case at about 190 and 280 K and in the second case at $\sim$ 420 K (Fig. 3). The dependence of the OSTL efficiency on the

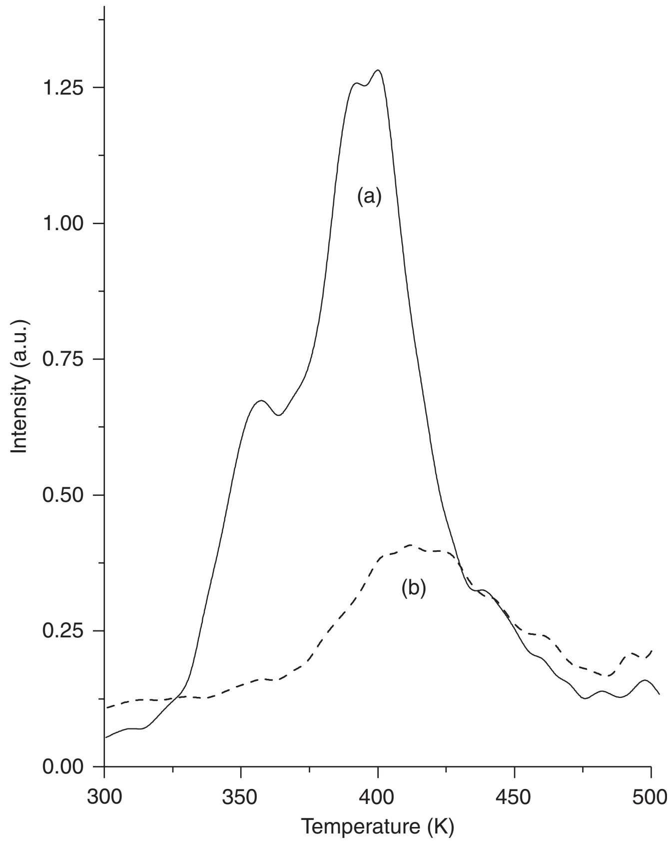

Fig. 4. Effects of prolonged exposure of an irradiated zircon crystal to 425 nm light at RT: (a) TL curve recorded immediately after irradiation at RT and (b) TL of irradiated crystal, but recorded after 30 min illumination with 425 nm light at RT.

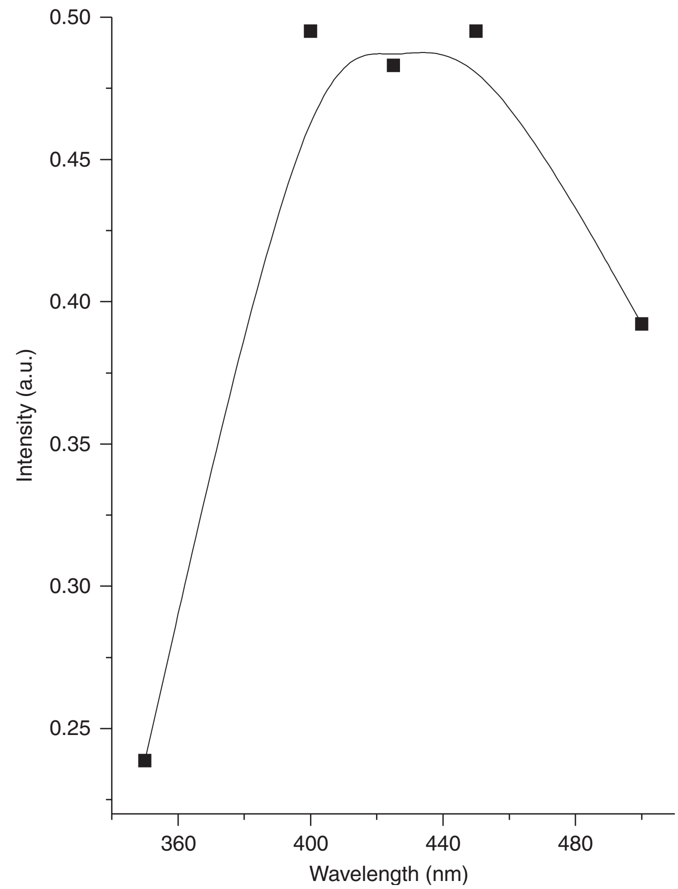

Fig. 5. Dependence of the TL intensity in the 300–450 K region on the wavelength of optical bleaching at RT (the TL of the irradiated sample was measured after 30 min illumination with light of various wavelengths).

wavelength of the stimulating light was also investigated. The OSTL stimulation spectra were measured for both the above-mentioned cases and showed for the low temperature OSTL peaks (first case) a maximum at $\sim$ 294 nm and for the OSTL peaks above RT (second case) at $\sim$ 425 nm. The conclusion that these glow peaks of zircon are due to a process of optical stimulation was supported by the finding that the wavelengths of stimulation were also most efficient for optical bleaching. Effects of prolonged RT illumination with 425 nm light, which was found to be most efficient for the optical stimulation at RT, are shown in Fig. 4. It can be seen that the exposure to 425 nm light at RT caused a strong decrease in the intensity of TL peaks above RT, while no notable decrease was recorded in the dark even after several hours. Prolonged illumination with the wavelength of 294 nm, which was most efficient for stimulation of the low temperature OSTL, also caused a strong decrease in the intensity of the original TL peaks. This effect of optical bleaching is apparently due to a depletion of carriers in the radiation-induced trapping states. The dependence of the optical bleaching efficiency on the wavelength was investigated as well and the results are shown in Fig. 5. Optical stimulation with 294 nm was also efficient in samples which were β irradiated at RT subsequently heated to about 1000 K, then cooled and illuminated with 294 nm at LNT. These results indicate a high temperature stability of the radiation-induced trap which is responsible for the 294 nm stimulation maximum, while the radiation defects which are responsible for the 430 and 255 nm absorption bands could be thermally annealed at about 800 K.

The OSTL method is known in various materials such as CaF_2, quartz extracted from pottery and aragonite to have important advantages for dosimetry over the common TL method (e.g. Bailiff et al., 1977). This method appears to have also some advantages for dating these zircon crystals, this in particular due to the fact that the main TL peaks above RT appeared at relatively low temperatures of 354 and 385 K and the higher temperature peaks are by 1–2 orders of magnitude weaker. The 354 and 385 K peaks are obviously due to fast thermal fading when kept at ambient temperature. The application of the OSTL method may therefore be more useful especially when cooling the sample just before the measurement and illuminating it with appropriate wavelength at LNT. The 190 and 280 K OSTL peaks were found to have a relatively high intensity.

In the present work, OSTL emission spectra were also measured and compared to the XL and TL emissions of the same zircon samples and the results are shown in Figs. 6a and b. It can be seen that the same emission bands near 350 and 420 nm appear in the XL as well as in various TL and OSTL peaks, indicating that the same luminescence centers are involved in

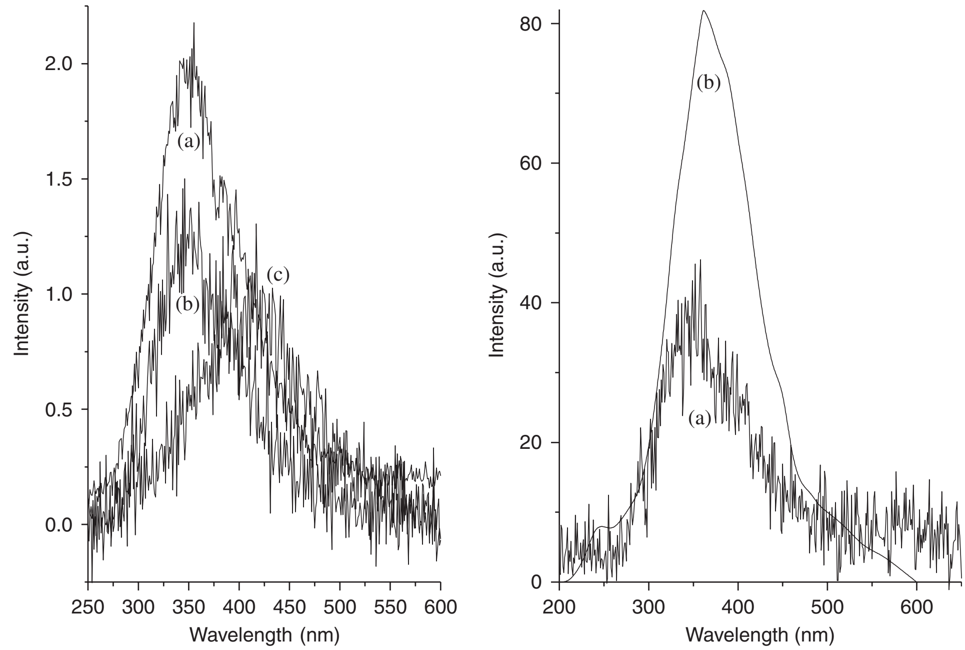

Fig. 6. (a) Emission spectra of zircon, recorded at: (a) 190 K TL peak, (b) 190 K OSTL peak, and (c) 280 K OSTL peak. (b) Emission spectra of a zircon crystal at: (a) 420 K OSTL peak and (b) XL at RT.

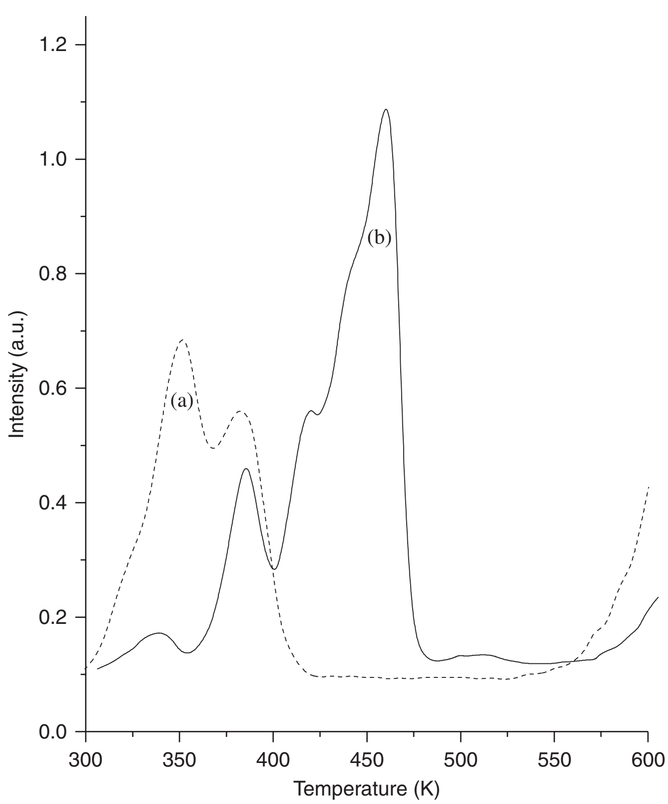

Fig. 7. Comparison of TL sensitivity of: (a) zircon (enlarged × 10) and (b) TLD-100.

the different emissions. The dependence of the TL and OSTL intensities on the radiation dose was also investigated. The TL intensity of the main 355 and 385 K peaks showed linear dose dependences up to β doses of about 2000 Gy. The dependence of the OSTL was measured for increasing β doses, subsequent heating to about 460 K and exposure to illumination with light of a constant time, wavelength and light flux. The OSTL intensity showed also a nearly constant dependence up to β doses of $\sim$ 2000 Gy. A comparison of the TL sensitivity of zircon to that of LiF:Mg,Ti (TLD-100) showed that the sensitivity of the main TL peaks in the 350–400 K region was about $\frac{1}{10}$ of that of the known TLD-100 phosphor (Fig. 7); while the sensitivity of the higher temperature TL peaks was 1–2 orders of magnitude lower.

4. Conclusion

The results of these experiments have shown that: the TL has excitation maxima in the VUV at 140 and 190 nm, and at the long wavelength tail of the fundamental absorption. The same traps are responsible for the TL induced by VUV as by or X or β irradiation. Deep traps, which are induced or filled by the different types of ionizing radiation, can be emptied by near UV or visible light of appropriate wavelength. The same wavelengths which were most efficient for stimulation of the OSTL, also caused an optical bleaching. The same luminescence centers are involved in the OSTL as in the TL and XL emission. These zircon crystals may have some advantages for application in TL or OSTL dating due to the content of radioactive impurities. The TL sensitivity of the main TL peaks below 400 K was about $\frac{1}{10}$ of that of TLD-100, and the sensitivity of the higher temperature TL peaks was 1–2 orders of magnitude lower. The lower temperature TL peaks are obviously subject to fast thermal fading at ambient temperature. The application of the OSTL method in these crystals may therefore be preferable to the regular TL method, in particular when using transfer from weaker but stable deep traps. The OSTL intensity has a nearly constant dependence up to β doses of ~ 2000 Gy.

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