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OPTICAL AND DOSIMETRIC PROPERTIES OF ZIRCON

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Irradiation effects were investigated in zircon crystals by methods of optical absorption and luminescence. Special attention was given to the effects of vacuum ultraviolet (VUV) radiation. The same main thermoluminescence (TL) peaks with the same thermal activation energies appeared after VUV as after X- or beta irradiation, indicating that the same traps were induced by the different irradiations. TL excitation spectra in the VUV showed an increase <220 nm and maxima near 190 and 140 nm. Excitation spectra of phototransferred TL (PTTL) and optically stimulated luminescence (OSL) were also measured. Most TL emission bands also appeared in the X-luminescence, PTTL and OSL. Dosimetric properties such as the TL radiation sensitivity, thermal stability of radiation-induced defects and TL dose dependence were also investigated. The radiation sensitivity of zircon was by an order of magnitude lower than that of TLD-100. The 355 K TL peak showed linear dose dependence only up to ∼500 Gy and the 520 K peak up to ∼1800 Gy.

INTRODUCTION

Radiation effects as well as photoluminescence (PL), X-luminescence (XL) and thermoluminescence (TL) in zircon have previously been studied by various authors[1,2]. Optical absorption of zircon has previously been measured in relatively few works and mostly dealt with absorption in the IR region[3]. In a recent theoretical study, the band gap of zircon ($ZrSiO_4$—containing 16.7 at% Zr) has been calculated and by applying a raw local density approximation (LDA) method a value of 4.58 ev (270 nm) was obtained; the application of a corrected LDA method resulted in a value of 7.95 ev (156 nm)[4]. In an experimental study a different value of 300 nm was mentioned as of cutoff wavelength[3]. Some studies in zircon are connected with its possible use in solid-state lasers. Due to its internal radioactivity, natural zircon has some advantages over the commonly used quartz for application in TL dating. A part of the studies concentrates therefore on the use of zircon in TL dosimetry and in dating of sediments. Some 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[2].

Most of the previous work on radiation effects dealt with effects of higher energy radiation such as gamma, beta or X-rays and only relatively few works dealt with vacuum ultraviolet (VUV) radiation. It has previously been shown that in various broad band crystals, the application of monochromatic VUV radiation can supply important information about the energy levels most efficient for defect formation[5,6].

In the present work irradiation effects were studied in natural zircon crystals. Special attention was given to monochromatic VUV radiation and the results were compared to those induced in the same samples by X- or beta radiation. Methods of optical absorption, XL, PL and TL as well as those of optically stimulated luminescence (OSL) and of phototransferred TL (PTTL) were applied for these investigations. Dosimetric properties were also studied in the present work. For application of a material as a TL, PTTL or an OSL dosemeter, certain properties are of importance. These are the luminescence efficiency, the temperature of the main TL peaks, the wavelength of the emission, the thermal stability and the temperature of thermal annealing, the reproducibility of results and linearity of dose dependence of the TL intensity over a wide range of doses. These properties were therefore also studied in the present work. The TL sensitivity and dose dependence were compared with those of TLD-100 and of some other recently investigated materials[7].

MATERIALS AND METHODS

The natural zircon crystals used for the present measurements were from Yakutia and were cut here to appropriate sample size. These Yakutia zircon crystals are known to have distinctive traces of radioactive elements such as uranium[3]. The X-irradiations were performed with a W-tube (40 kV, 15 mA) and the beta irradiations with a ^{90}Sr source of a 1.5 Gy min^{-1} dose rate. The optical absorption was measured with a Cary 17 spectrophotometer in the 200–1000 nm region and at shorter wavelengths with a 1 m normal-incidence

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VUV monochromator. The far UV irradiations in the 120–200 nm region were also carried out with this VUV monochromator and an H_2 arc lamp. The X- and UV irradiations were carried out at various temperatures between 80 and 300 K. The TL measurements above room temperature (RT) up were carried out in a TL compartment flushed by N_2 gas; the heating rate above RT was 5 K s^{-1}. For the low temperature TL and PTTL measurements, the samples were kept in a liquid nitrogen vacuum cryostat and heated at a rate of 20 K min^{-1}. The OSL was stimulated at various temperatures between 80 and 400 K by monochromatic UV light. The PL, OSL, TL and PTTL measurements were taken with Aminco-Bowman/2 luminescence-spectrometer.

RESULTS AND DISCUSSION

Optical absorption

Absorption measurements in the 1000–200 nm region showed a weak absorption band near 325 nm and a sharp increase of optical density (OD) below ~225 nm, resembling the onset of the fundamental absorption. Independent absorption measurements in the VUV region showed the same sharp increase of OD below ~225 nm and additional bands near 190, 175, 155 and 140 nm (Figure 1). This experimentally measured wavelength of 225 nm (5.5 ev) does not agree with any of the two theoretical values of 4.58 and 7.95 ev for the band gap of zircon, which were recently calculated by Kawamoto *et al.*[4], by applying a 'raw' and a 'corrected' LDA method, respectively. After prolonged X- or beta irradiation at RT, additional absorption bands appeared at 430 and 255 nm; both these bands were annealed by heating to ~800 K.

Luminescence and thermoluminescence

During first heating of the sample, TL peaks were recorded at about 400, 425, 520 and near 640 K even without any irradiation; this TL is apparently due to radioactive impurities in these natural crystals. Samples that were X- or beta irradiated in the laboratory at RT showed a notable TL during heating; the main peaks appeared at 354, 385 K and the weaker ones at 520 and 640 K. After LNT irradiation, the main peaks appeared at 158, 256, 267, 335 and 374 K. TL could also be excited with monochromatic VUV radiation. Excitation spectra of the TL in the UV region showed a strong increase at the long wavelength tail of the fundamental absorption <220 nm and maxima near 190 and 140 nm. (Figure 2). In Figure 3, the TL glow curves induced at RT by monochromatic VUV radiation and by beta radiation are shown. The comparison of the results obtained after monochromatic VUV with those obtained by beta or X-irradiations showed that essentially the same main TL peaks with the same thermal activation energies appeared in the zircon crystals after VUV as after the higher energy irradiations, indicating that the same traps were induced by the different irradiations (Figure 3). This fits analogous results, previously obtained in various other crystals[5,7].

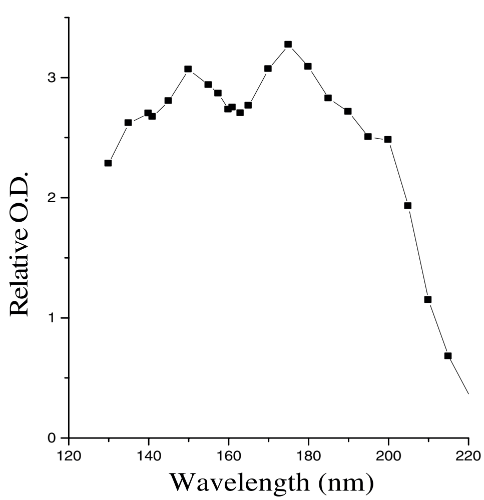

Figure 1. Absorption of zircon crystal in the VUV region at LNT.

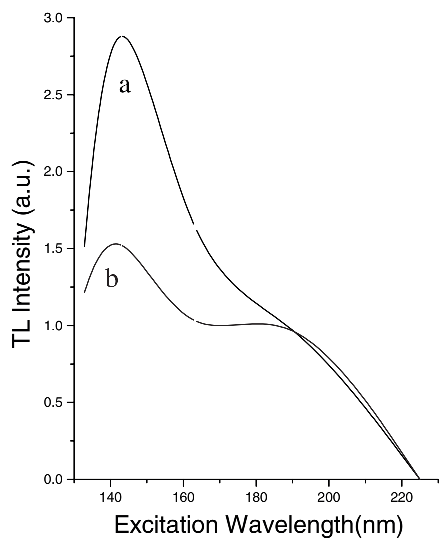

Figure 2. TL excitation spectrum of zircon in the VUV region (a) at LNT and (b) at RT (×2).

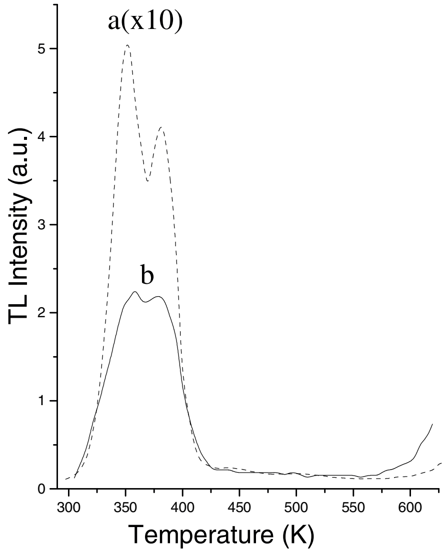

Figure 3. TL induced at RT by (a) VUV irradiation (180 nm) and (b) beta radiation (reduced one-tenth).

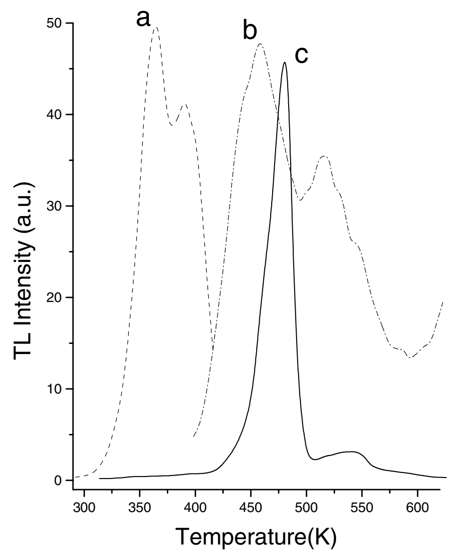

Figure 5. Comparison of TL sensitivities at constant beta doses of 90 Gy at (a) lower temperature peaks of zircon (enlarged $\times 10$), (b) higher temperature peaks of zircon (enlarged $\times 100$) and (c) LiF:Mg,Ti (TLD-100).

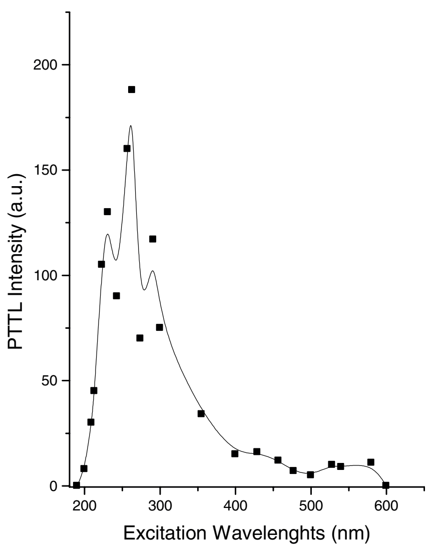

Figure 4. Excitation spectrum of the 276 K PTTL peak, recorded after beta irradiation at RT and subsequent optical stimulation at LNT. (The solid line represents a computer best-fit to the experimental results.)

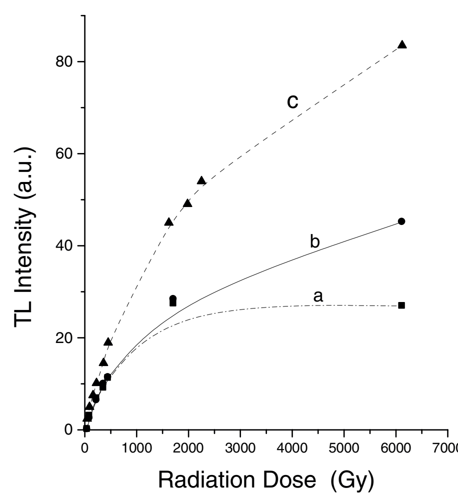

Figure 6. Dependence of TL intensity on radiation dose in the 0 to ~7000 Gy region recorded at (a) 355 K peak (b) 385 K peak and (c) 520 K peak (enlarged $\times 5$).

In samples, which had previously been exposed to ionising radiation, TL and PL could also be excited by illumination with longer wavelengths that could not excite any PL or TL in non-irradiated samples; the wavelength of 294 nm was most effective for these excitations. These emissions are therefore attributed to processes of OSL and PTTL; this is also supported by the fact that prolonged illumination with 294 nm light caused a sharp decrease of the original glow peak intensities, which is apparently due to a phototransfer of the trapped carriers and the emptying of the deep traps. The wavelength of 294 nm was most effective for stimulation of some OSL bands, but the 645 nm OSL emission could also be stimulated by 470 nm light.

The spectral decomposition of the TL emission recorded at the low temperature TL peaks of these Yakutia zircon crystals showed a main emission band at 320 nm and additional bands at 350, 385 and 480 nm. Above RT, the 350 nm emission was dominant. The XL at RT showed main bands at 355 nm and weaker bands at 235, 480, 575 and 750 nm. At LNT the emission was by an order of magnitude stronger and the main band was at 280 nm and the weaker ones at 355 and 450 nm. The PL also showed emission bands at 350, 390 and 450 nm.

Dosimetric properties

Dosimetric properties such as the TL radiation sensitivity, the thermal stability of the radiation-induced defects as well as the TL dose dependences were also investigated in the present work. The TL 354 K peak was found to be the main peak at low doses but at higher ones the 385 and 520 K peaks became dominant. The radiation sensitivity was also compared to that of known TL dosemeters and was found to be by an order of magnitude lower than the sensitivity of the well-known LiF:Mg, Ti (TLD-100) phosphor (Figure 5) and of $CsGd_2F_7:Pr^{3+}$ and by about two orders of magnitude lower than that of $KMgF_3:Eu^{2+}$ and of $SrF_2:Pr^{3+}$. The lower temperature peaks showed linear dose dependence up to ~500 Gy only and a tendency to saturation for higher doses that is probably due to a simultaneous process of thermal fading. The higher temperature peak at 520 K showed nearly linear dose dependence up to ~1800 Gy (Figure 6).

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