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Thermoluminescence properties of natural zoisite mineral under γ-irradiations and high temperature annealing

H. Javier Ccallata*, L. Tomaz Filho, S. Watanabe

Departamento de Física Nuclear, Instituto de Física, Universidade de São Paulo, Rua do Matão, travessa R, 187, CEP 05508-900, São Paulo, SP, Brazil

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ABSTRACT

Natural silicate mineral of zoisite, $Ca_2Al_3(SiO_4)(Si_2O_7)O(OH)$, has been investigated concerning γ-radiation, UV-radiation and high temperature annealing effects on thermoluminescence (TL). X-ray diffraction (XRD) measurement confirmed zoisite structure and X-ray fluorescence (XRF) analysis revealed besides Si, Al and Ca that are the main crystal components, other oxides of Fe, Mg, Cr, Na, K, Sr, Ti, Ba and Mn which are present in more than 0.05 wt%. The TL glow curve of natural sample contains (130–150), (340–370) and (435–475) °C peaks. Their shapes indicated a possibility that they are result of composition of two or more peaks strongly superposed, a fact confirmed by deconvolution method. Once pre-annealed at 600 °C for 1 h, the shape of the glow curves change and the zoisite acquires high sensitivity. Several peaks between 100 and 400 °C appear superposed, and the high temperature peak around 435 °C cannot be seen. The ultraviolet radiation, on the other hand, produces one TL peak around 130 °C and the second one around 200 °C and no more.

1. Introduction

Zoisite of chemical formula $Ca_2Al_3(SiO_4)(Si_2O_7)O(OH)$ is a sorosilicate, one of the members of the epidote group. The crystal structure is orthorhombic, space group *Pnma* and a hardness little above 6 in the scale of Moh. Several structural studies of natural and synthetic zoisites of different regions indicate that the principal feature is a double tetrahedron (Si_2O_7) that links two types non-equivalent octahedral chains M1,2 and M3. The M1 octahedra form endless, edge sharing single-chains parallel [0 1 0] to which individual M3 octahedra are attached exclusively on one side. As the monoclinic forms, the octahedral chains are across linked in [1 0 0] and [0 0 1] by isolated SiO_4 tetrahedra and Si_2O_7 groups with two non equivalent large A1 and A2 positions in between (Fig. 1). The lattice constants of zoisite are $a = 16.15–16.23$ Å, $b = 5.51–5.581$ Å and $c = 10.0229–10.16$ Å [1–4].

Ions of Fe^{3+} and Cr^{3+} that enter by aluminum in the structure are replacements more important in zoisite. On the other hand, monovalent cations such as lithium, sodium and potassium are in interstitial positions outside the tetrahedrons and octahedrons. Electron Paramagnetic Resonance (EPR) studies on Mn-rich zoisite (thulite), indicated that the Mn replaces ions of Al and Fe^{3+} ions are in tetrahedral and octahedral sites [5].

EPR studies carried out by Tsang and Ghose [6,7] have related the anisotropic EPR line, observed at low magnetic fields, in blue zoisite (tanzanite) as being due to Fe^{3+} ion that enters as impurity in the structure of the crystal, substituting Al in position II of the octahedral chains. In a similar EPR study, Hutton [8] has given a different interpretation. The ion of Cr^{3+} was considered to be responsible for EPR line in the low field region of the spectrum. Transitions for the case of substitution at the Al sites in the octahedral chains induce a change of g factor from 2 to 4 for the transition $-1/2$ to $+1/2$ of a system of spin $S = 3/2$. This change in g factor can be caused by very intense Crystal Field in an octahedral environment of low symmetry.

Studies of optical absorption made by Schmetzer and Berdesinski [9] in zoisite sample with high content of Cr has attributed the bands in 662 and 458 nm as being of the Cr^{3+} in a octahedral environment. On the other hand, Koziarska et al. [10] studied the natural tanzanite with high concentrations of $V^{2+/3+}$ and Cr^{3+} with regard to Fe and Mn. Their results indicated that Cr^{3+} ion is responsible for the luminescence in the blue tanzanite. Additionally it was shown that the ample luminescent spectrum in the infra-red region suggest that the zoisite is interesting material for laser applications.

As zoisite is an epidote mineral its EPR, thermoluminescence (TL) and optical absorption (OA) spectra are expected to be somewhat similar to those of other members of this group. However, specifically for zoisite no TL works were found in the literature.

* Corresponding author. Tel.: +55 11 3091 6990.
E-mail addresses: henrysjc@gmail.com (H.J. Ccallata), watanabe@if.usp.br (S. Watanabe).

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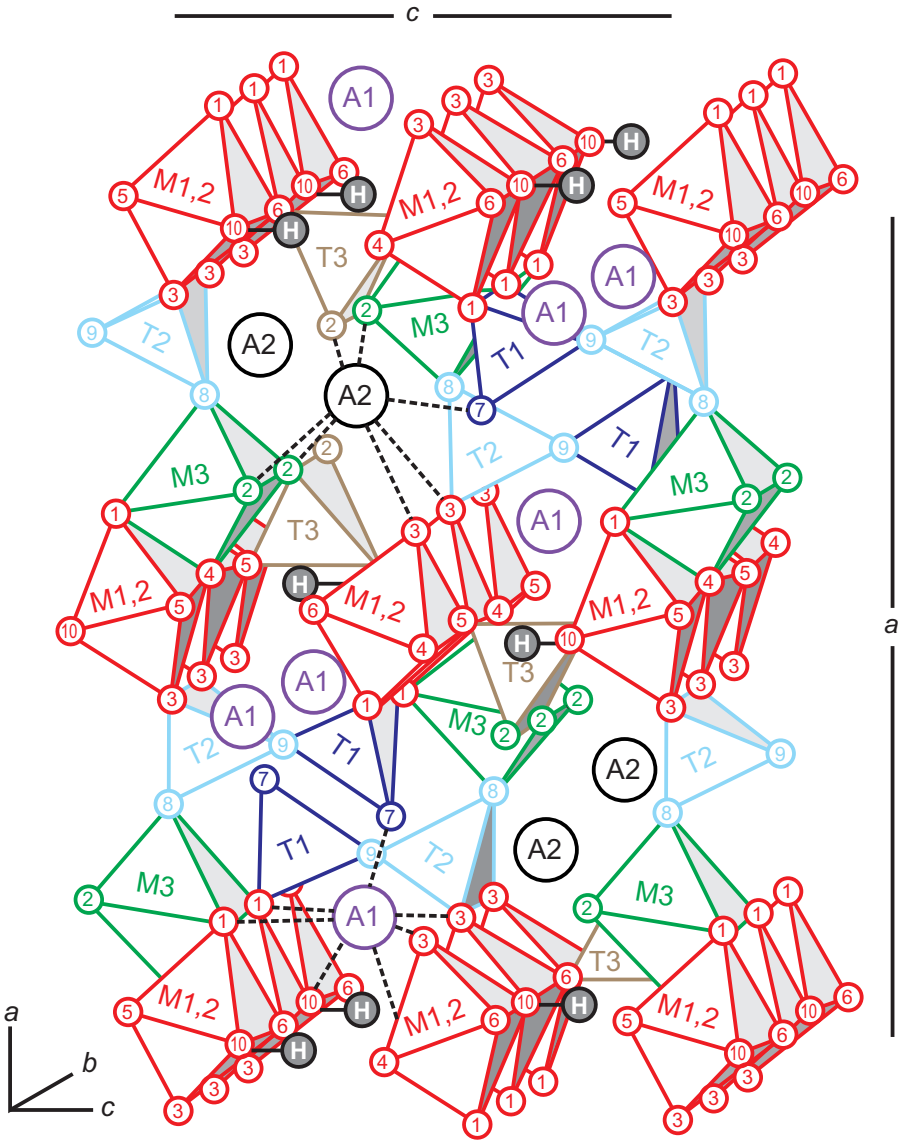

Fig. 1. Linkage of M-octahedra and T-tetrahedra in zoisite. Dashed lines show the nearest oxygen neighbors of the A positions which form the A1 and A2 polyhedrons [2–4].

The work that has more relationship with our is the study by Khalifa et al. [11], who studied the TL properties of minerals sphene and epidote under radiation damages without heat treatments. Both minerals exhibit complex glow curves with several overleaping peaks. For epidote, three peaks at 92, 114 and 122 °C were found. Here the experimental glow curve was studied using the T_m–T_{STOP} thermal cleaning procedure. This method is appropriate to find peak positions with high intensity in complex TL glow curves.

The effect of annealing at 600 °C for 1 h on TL properties of epidotes from Tyrol and Norway seems to decrease the amount of UV bleaching besides enhancing the TL sensitivity of the samples [12]. It was assumed that TL emission in the epidote may be due to the diffusion of defects; these are responsible for luminescence resulting in an enhancement of the probability of radiation transition. This sensitization of thermoluminescence with annealing is in accord with earlier reports on similar effects on zircon and apatite [13,14].

In this work, TL properties of zoisite under high temperature annealing, gamma and UV irradiation effects have been studied by TL glow curve analysis. Additionally, we have determined the number of peaks in the glow curve and the TL parameters (E and s) of each peak. A model for the observed TL emission has been proposed based on thermal annealing behavior Al, Ti and E'_1 centers.

2. Experimental

Natural zoisite, used in this work, was obtained at Teófilo Otoni in the state of Minas Gerais – Brazil. Intense green color of the sample is due to the high quantity of Cr in the structure. Crystals of zoisite were ground into powders keeping grains of the size between 0.080 and 0.180 mm. Grains smaller than 0.080 mm were used in the X-ray fluorescence and X-ray diffraction analysis. A ^{60}Co source with a dose rate of 2.04 kGy h^{-1} was used for gamma irradiations.

TL glow curves were obtained using a Daybleak 1100 series automated TL reader system equipped with a photomultiplier EMI 9235QA and they were recorded from 50 °C up to 500 °C with a heating rate of 4 °C s^{-1} in nitrogen atmosphere. The TL light spectrum was obtained in a home made TL reader with EMI 9789QB photomultiplier and UNICROM 100 monochromator. For the ultraviolet irradiation a calibrated 60 W Hg lamp was used and the powder samples exposed for several time intervals at 15 cm of distance between lamp and sample inside a closed chamber. All gamma,

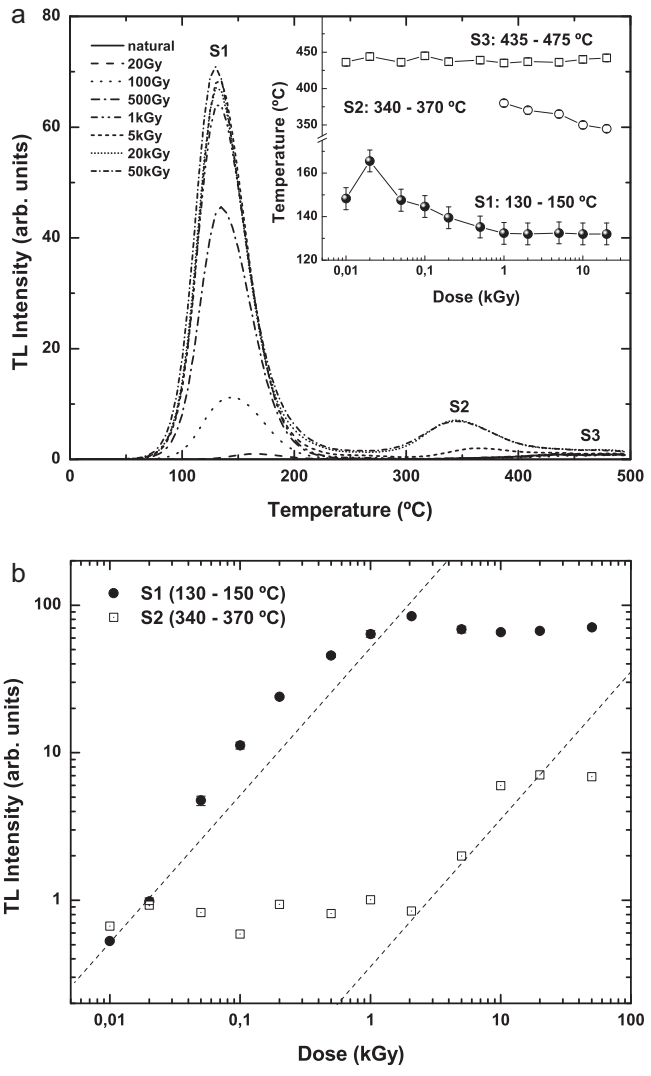

Fig. 2. (a) TL glow curves of natural zoisite with additional gamma doses. Inset: the peak temperatures of glow peaks as a function of irradiation determined from the maximum points of glow peaks. (b) TL response vs radiation doses for peaks S1 (130–150 °C) and S2 (340–370 °C).

ultraviolet irradiations and TL measurements were carried out at room temperature (RT).

3. Results and discussion

Chemical analysis using X-ray fluorescence showed that the natural zoisite from Teófilo Otoni contains the following main oxides: SiO_2 (40.2) mol%, Al_2O_3 (23.2) mol%, CaO (25.1) mol%. Besides the main components, Fe_2O_3 (2.87), MgO (2.55), Cr_2O_3 (1.21), NaO (0.90), K_2O (0.28), SrO (0.19), TiO_2 (0.14), BaO (0.13) and MnO (0.06), in mol%, are present in the crystal structure as impurities. The diffractograms of the natural zoisite and samples that had been annealed at 500, 600, 700, 800 and 900 °C for 1 h confirmed that it is zoisite crystal.

The TL response of natural zoisite as a function of γ-irradiation in the interval from 0.010 to 50 kGy is shown in Fig. 2a. The glow curves are characterized by three peaks: S1 (130–150 °C), S2 (340–370 °C) and S3 (435–475 °C). Inset of Fig. 2a shows the change of the central position of peaks S1 and S2 from high to low temperature when the dose of γ-irradiation increases. This behavior indicates that both S1 and S2 are composed by two or more peaks strongly superposed. The position of the peak S3 in

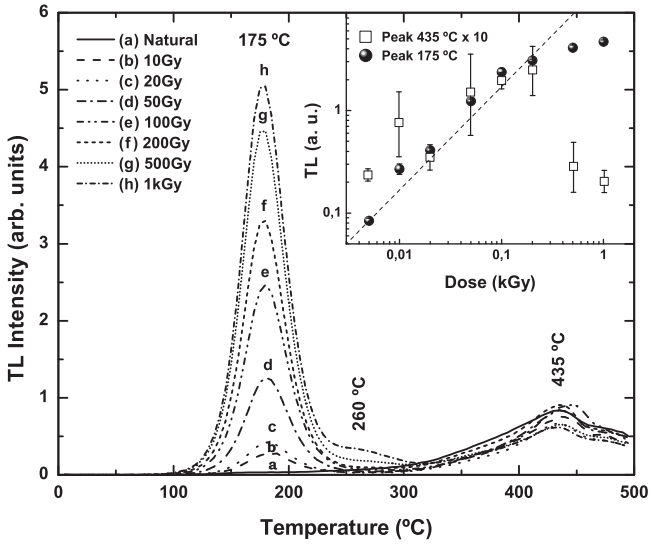

Fig. 3. TL glow curves of natural zoisite pre-annealed at 150 °C before completing the TL measurement.

high-temperature shows small change and may be considered constant.

A quantitative analysis of the TL intensity of peaks S1 and S2 shows that both have a supralinear behavior as function of dose, i.e. from 20 Gy to 100 Gy for S1 and 2 kGy to 10 kGy for S2 (Fig. 2b). TL intensity of saturation of these peaks occurs at 2 kGy and 10 kGy respectively.

In order to eliminate the peaks at low-temperature, which in general are more unstable, a thermal cleaning before completing the TL reading was performed up to 150 °C. Fig. 3 shows two peaks at 175 °C and 435 °C that saturates around 100 Gy and 50 Gy respectively. Additionally, a peak around 260 °C becomes visible only from 200 Gy.

The effect of annealing at high-temperature (500–900 °C) on the natural samples before irradiation with 1 kGy is shown in Fig. 4. In the figure, a maximum enhancement of TL response is observed for annealing between 600 °C and 700 °C. From the figure it can be noticed that the TL peaks below 200 °C are growing up to a maximum of emission at 700 °C and from then onwards, they are found to decrease in intensity. The behavior of all peaks in the region of

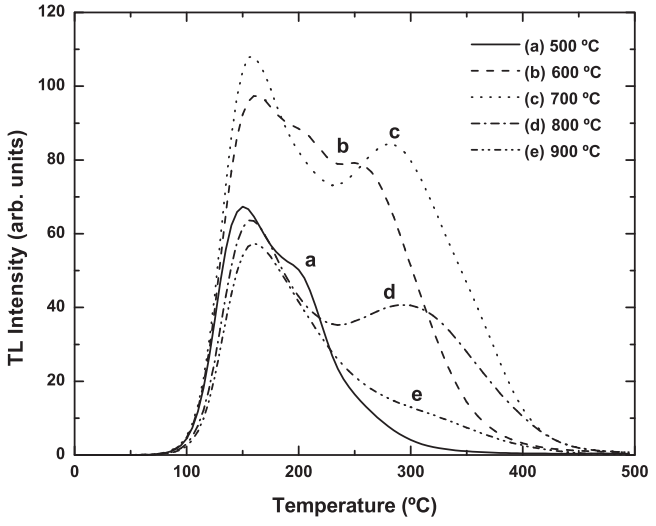

Fig. 4. Effect of high temperature annealing before irradiation. After annealing samples were irradiated to 1 kGy gamma dose.

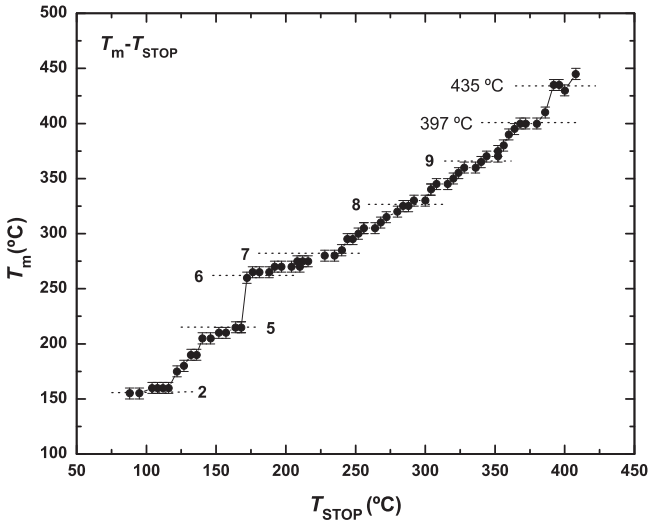

Fig. 5. Results of the T_m–T_{STOP} measurements for the zoisite annealed at 600 °C and irradiated to 1 kGy gamma dose. The flat regions mark the presence of individual peaks and give estimates of their positions (T_m values).

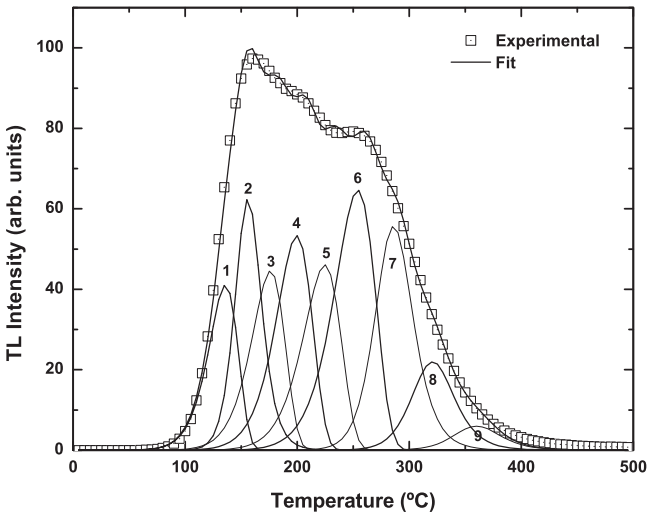

Fig. 6. TL glow curve of the zoisite annealed at 600 °C and irradiated to 1 kGy gamma dose, and them submitted to deconvolution. The peaks at 397 and 435 °C because of their low intensity were not included in the deconvolution.

200–400 °C is different; a definition of the number of peaks that participate is difficult as both, TL intensity and temperature position show an unusual change. In particular may be noticed that for annealing in the region between 800 and 900 °C the TL intensity is significantly reduced.

This result is very different from those observed in other silicate minerals by other authors and also those investigated in our laboratory [15–17]. According to literature, the TL emission in silicate minerals, independent of type and amount of impurities, grows up to a maximum TL intensity for annealing around 900 and 1000 °C. On the other hand, TL results similar to ours were found by Al-Khalifa et al. [12] with the epidote mineral. This is understandable since zoisite is one of the members of the epidote group. This suggests that TL sensitization in minerals of this group is due to the ion exchange Al-Fe or Al-Cr in the basic structure of crystal.

3.1. TL peak parameters determination

To find not only the *E*-value (activation energy) but also possible number of TL peaks, we opted for McKeever's T_m–T_{STOP} method and Computerized Glow Curve Deconvolution (CGCD) method [18,19].

Fig. 5 shows the result of T_m–T_{STOP} method applied to a sample of zoisite annealed at 600 °C for 1 h and then irradiated with 1 kGy gamma dose. In the figure the flat regions indicate the position of each peak. Peaks around 150 °C, 225 °C, 255 °C, 397 °C and 435 °C can be observed.

Using the TL program, which analyzes individual TL glow peaks and its TL parameters through the CGCD method, deconvolution was carried out for the glow curve [20].

As often happens a large number of peaks is found, namely, between 100 °C and 400 °C, and nine peaks are necessary to fit the experimental glow curve (Fig. 6). Activation energy – *E*, factor frequency – *s* and order kinetics – *b* of each peak are listed in Table 1. Note that peak P1 does not appear in the T_m–T_{STOP} profile (Fig. 5) and it was found by TL reading of a natural sample irradiated with 1 kGy and read after 2 weeks and 2 years respectively (Fig. 7). This figure shows the fading effect of natural sample and makes valid the hypothesis that the peak S1 is composed by peaks at 130 and 150 °C. The TL parameters (*b*, *E* and *s*) calculated here are in complete agreement with our previous work with zoisite under beta irradiations [21].

Table 1
Energy (*E*), frequency factor (*s*), temperature (T_m) and order of kinetic (*b*) for each TL peak in zoisite.

Peak	*b*	T_m (°C)	*E* (eV)	*s* (s^{-1})
1	1	130	1.08 (5)	$5.56\,(72)\times10^{12}$
2	2	150	1.97 (5)	$1.26\,(62)\times10^{13}$
3	1	175	1.14 (4)	$1.74\,(98)\times10^{12}$
4	1	200	1.18 (4)	$9.70\,(41)\times10^{11}$
5	1	225	1.24 (5)	$7.69\,(40)\times10^{11}$
6	1	255	2.17 (4)	$2.63\,(73)\times10^{10}$
7	2	285	2.28 (3)	$2.34\,(82)\times10^{9}$
8	2	320	2.30 (5)	$2.88\,(90)\times10^{9}$
9	2	360	2.32 (6)	$1.00\,(63)\times10^{9}$

The same sample used in the deconvolution analysis was irradiated with additional doses between to complete 20 kGy of dose. Fig. 8 shows the glow curves behavior and TL vs dose analysis of peaks P2, P4 and P6 respectively. A linear increase is observed for 155 °C and 200 °C peaks but the peak at 255 °C grows linearly from

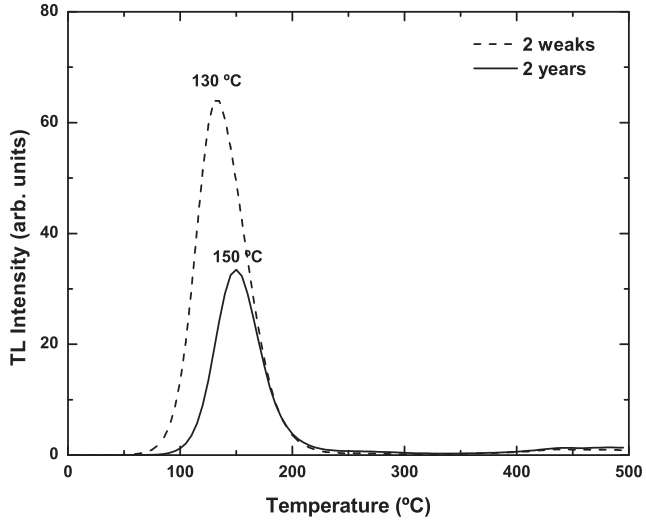

Fig. 7. Fading of TL signal in sample irradiated with 1 kGy of dose and read in two different times. Shift of position peak S1 indicate that its composed by two individual peaks around 130 and 150 °C.

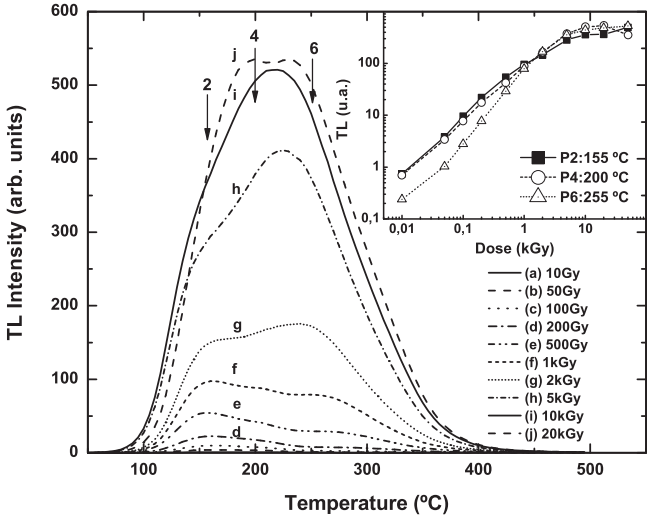

Fig. 8. Glow curves of peaks 2, 4 and 6 for irradiations between 10 Gy and 20 kGy using linear heating rate of 4 °C s^{-1}. Inset: TL vs dose curves for 155, 200 and 255 °C peaks.

10 to 50 Gy then supralinearly up to about 1 kGy. Beyond this dose-value all peaks start to saturate.

The TL emission spectrum of zoisite in 3D and 2D representation (Fig. 9a and b) shows a strong band around 310 nm and weak one at 270 nm. This indicates that there exist two recombination centers. It is clear that the most of recombination of centers occur at 310 nm.

The effect of UV bleaching is shown in Fig. 10a. In this case, samples annealed at 600 °C for 1 h and then irradiated to 1 kGy were exposed to UV light from calibrated 60 W mercury lamp. In first place, in the sample not exposed to UV light, peaks around 130, 200 and 255 °C are visualized. At this stage peak P6 (255 °C) is more than 3 times weaker than peak P4 (200 °C). Anyway the peak height of all of them decreases as the time of bleaching increases. Fig. 10b shows the decay curves with UV exposure time of the above three peaks. They seem to obey an exponential equation:

$$I(t) = I_r + I_0 \exp\left(\frac{-t}{\tau}\right) \quad (1)$$

where I_r is the residual TL-value, I_0 is the TL intensity at $t = 0$ and τ the time after which TL intensity minus the residual-value is 30% of I_0-value. From this result we can say that all three peaks are bleached in short time, about 3–4 min and they all leave a residual TL, namely, the UV light does not bleach completely. On the other hand, the result shown in Fig. 10a is difficult to understand since a very long exposure of 3900 min shows a much smaller TL residual. It is necessary to perform further bleaching measurements for exposure times between 120 and 3900 min to understand this result.

In many silicate minerals already examined, transition metal ions, commonly found, give rise to absorption band and EPR signals which are independent of radiation as well as of annealing temperature. Therefore, TL mechanism cannot be based on such impurities. On the other hand, aluminum, titanium, sodium, lithium, hydrogen and oxygen (this is not an impurity), are important elements that participate in the TL emission.

Aluminum is present in many silicate minerals (Ti not always, but nevertheless quite frequently), and always is found substituting Silicon in the tetrahedron SiO_4. Since Aluminum is trivalent (+) and silicon tetravalent (+), the charge disequilibrium is compensated by attracting monovalent ions such as Na^+, Li^+, H^+, giving rise to centers like $[AlO_4/M^+]$. In the case of titanium, $[TiO_4/M^+]$-center is formed. These two centers release M^+ under irradiation leaving

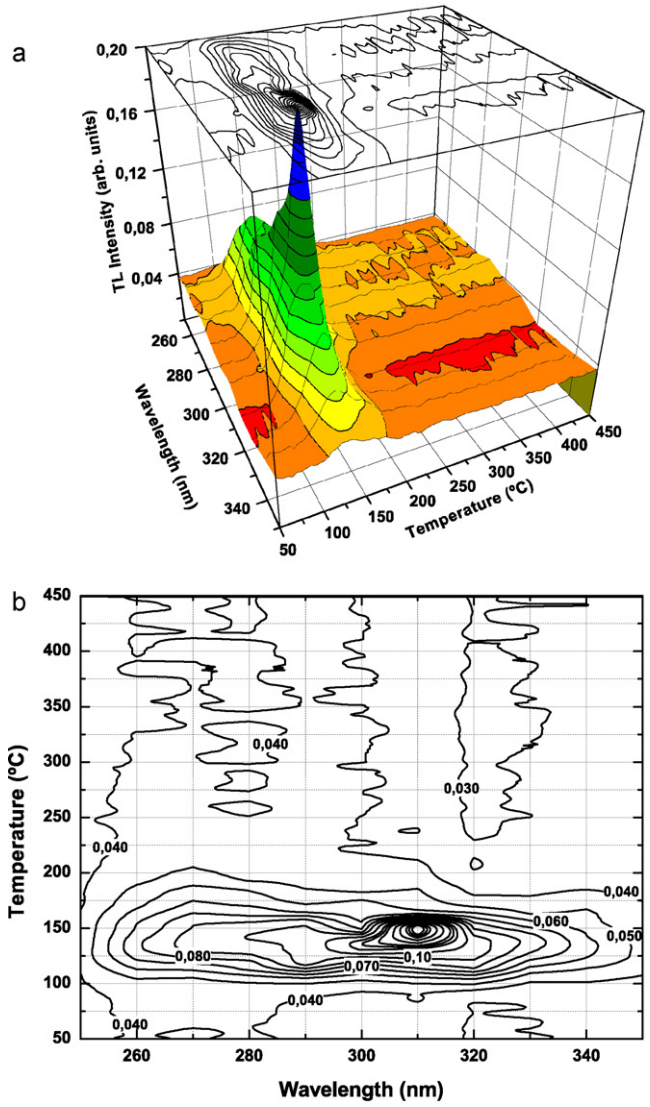

Fig. 9. The isometric plot of the TL emission spectrum of zoisite annealed at 600 °C followed by 1 kGy γ-ray irradiation. A heating rate of 4 °C s^{-1} was used. (a) 3D representation. (b) TL emission spectra contour map.

Al-hole center and Ti-hole center:

$$[AlO_4/M^+] + e^- \xrightarrow{\text{irradiation}} [AlO_4/h] + M(M^+ + e^-)$$

where $[AlO_4/h]$ is called aluminum-center.

Rudra and Fowler [22] have shown that in quartz oxygen vacancies can be produced thermodynamically at room temperature (RT); we will denote it by $[OV]^{2+}$. We expect that this also happens in any silicate crystal. Electrons released due to irradiation can be captured by oxygen vacancy forming $[OV/e^{2-}]$ center. Toyoda and Ikeya [23] have shown by ESR measurements that as the quartz crystal is heated from RT, by EPR measurements, Ti-center signal starts decreasing around 120 °C and disappear around 250 °C; the Al-center starts decreasing around 150 °C and disappears around 420 °C. The E'_1 center is observed to increase from 120 °C reaching maximum at 300 °C and then decreases and disappears around 450 °C. Of course, E'_1-center is $[OV/e^{2-}]$ that lost one electron.

We then interpreted Toyoda and Ikeya results in the following way for silicate of zoisite: Around 120 °C one electron from $[OV/e^{2-}]$-center is released giving rises to E'_1 center. The released electron recombines either with hole in Ti-center or with hole in Al-center and emits 130–150 °C and 200 °C TL peaks light. Beyond

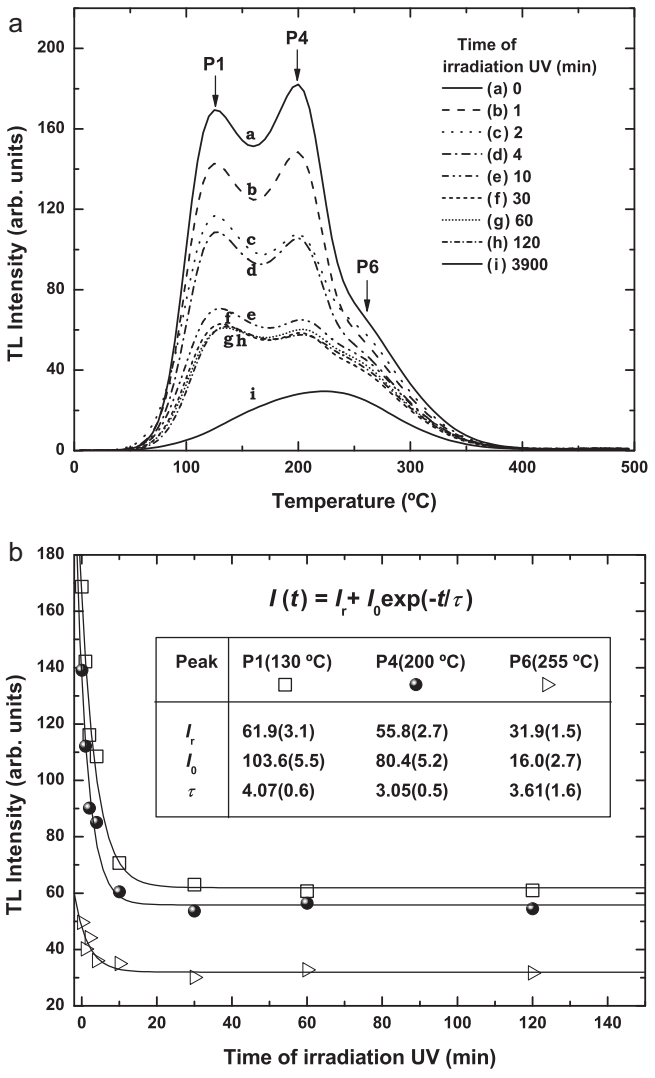

Fig. 10. Bleaching of TL peaks by UV light from 60 W mercury lamp in different times intervals. The samples were annealed at 600 °C and then irradiated to 1 kGy gamma dose and later exposed to UV light. (a) Resulting TL glow curves. (b) Decay curves for peaks at 130, 200 and 255 °C.

300 °C heating releases electron from E'_1 center and recombining with hole in Al-center emit light producing high temperature peak.

4. Conclusions

A natural zoisite sample irradiated from 10 Gy to 50 kGy of gamma radiation, presents a prominent TL peak in the range 130–150 °C, which is a superposition of 130 and 150 °C peaks. Much less intense peaks are observed at 340–370 °C and at 435 °C. Thermal cleaning at 150 °C isolates peak at 175° C.

Using the deconvolution analysis not less than nine peaks superposing and covering 100–400 °C temperature range are found, with *E*-value varying from 1.08 eV to 2.32 eV. The TL emission spectrum has shown a very strong band around 310 nm and a much weaker band around 270 nm indicating that there are two recombination centers.

Ultraviolet light causes bleaching of TL peaks of 600 °C in zoisite samples which have been annealed for 1 h and irradiated to 1 kGy gamma dose. The decrease of TL peaks occurs rather fast, In 3–4 min 65% of the intensity is diminished.

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References

[1] E. Fesenko, I. Rumanova, N. Belov, Doklady of the Academy of the Sciences of the USSR 102 (1955) 275–278.
[2] W.A. Dollase, American Mineralogist 53 (1968) 1882–1898.
[3] A. Liebscher, M. Gottschalk, G. Franz, American Mineralogist 87 (2002) 909–921.
[4] G. Franz, A. Liebscher, Reviews in Mineralogy and Geochemistry 56 (2004) 1–81.
[5] G. Srinivasulu, B. Madhu Sudhana, B.J. Reddy, Spectrochimica Acta Part A: Molecular Spectroscopy 48 (10) (1992) 1421–1425.
[6] T. Tsang, S. Ghose, Journal of Chemical Physics 54 (1971) 856–862.
[7] S. Ghose, T. Tsang, Science 171 (3969) (1971) 374–376.
[8] D.R. Hutton, Journal of Physics C: Solid State Physics 4 (10) (1971) 1251–1257.
[9] V.K. Schmetzer, H.W. Berdesinski, Neves Jahrbuch fur mineralogie Monatshefte 5 (1978) 197–202.
[10] B. Koziarska, M. Godlewski, A. Suchocki, M. Czaja, Z. Mazurak, Physical Review B 50 (17) (1994) 12297–12300.
[11] M. Khalifa, I. Al-Khalifa, S. Durrani, Radiation Protection Dosimetry 17 (1986) 407–410.
[12] I. Al-Khalifa, M. Khalifa, S. Durrani, International Journal of Radiation Applications and Instrumentation Part D: Nuclear Tracks and Radiation Measurements 13 (1987) 171–175.
[13] S. Durrani, Y. Amin, Nuclear Tracks and Radiation Measurements 10 (1985) 539–546.
[14] S. Durrani, Y. Amin, J. Alves, Nuclear Tracks and Radiation Measurements 8 (1984) 79–84.
[15] E.A. Gallegos, N.F. Cano, S. Watanabe, J.F.D. Chubaci, Radiation Measurements 44 (2009) 11–17.
[16] N.F. Cano, J.M. Yauri, S. Watanabe, J.C.R. Mittani, A.R. Blak, Journal of Luminescence 128 (7) (2008) 1185–1190.
[17] J.M. Yauri, N.F. Cano, S. Watanabe, Radiation Measurements 43 (8) (2008) 1331–1336.
[18] S.W.S. McKeever, Physica Status Solidi A 62 (1980) 331–340.
[19] G. Kitis, J. Gomez-Ros, J. Tuyn, Journal of Physics D: Applied Physics 31 (1998) 2636–2641.
[20] K.S. Chung, H.S. Choe, J.I. Lee, J.L. Kim, S.Y. Chang, Radiation Protection Dosimetry 115 (2005) 343–349.
[21] H. Javier Ccallata, S. Watanabe, AIP Conference Proceedings 1265 (1) (2010) 391–394.
[22] J.K. Rudra, W.B. Fowler, Physical Review B 35 (15) (1987) 8223–8230.
[23] S. Toyoda, M. Ikeya, Geochemical Journal 25 (6) (1991) 437–445.