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Electron immigration from shallow traps to deep traps by tunnel mechanism on Seydişehir aluminas

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ABSTRACT

In this study, the fading mechanism of Seydişehir alumina in Turkey, which is considered to be used for radiation dosimetric purposes, was investigated. The materials were first exposed to beta radiation and then stored in dark and dry ambient conditions at room temperature (RT) at previously desired storage periods. It was observed that the glow curve of Seydişehir alumina consists of four glow peaks between RT and 400 °C. The glow peaks (peaks 1, 2 and 3) between room temperature and 250 °C possessed very high levels of anomalous fading. However, the intensity of new glow peak at around 378 °C is highly increased with time. As a result of the experimental studies, it was concluded that the reason behind anomalous fading can be explained by means of tunneling (quantum tunneling) mechanism.

1. Introduction

An insulator and/or semi-conductor material absorbs energy when irradiated. This absorption causes some electrons to be elevated from the valence band to the conduction band and eventually leads to the generation of some free electron–hole pairs in the material. As a result of the movement of free electrons–holes at the conduction and valence bands, respectively, free charge carriers of opposite signs come across each other. Then they either recombine or get captured by trapping states formed either due to crystal defects or doped atoms. Trapped electrons stay in the traps for a while depending on the temperature of the material and activation energy of the trap level [1–6]. The half-life of a trapped charge carrier in a trap can be calculated by the following equation [2];

$$\tau = s^{-1} \exp(E_t/kT) \quad (1)$$

For example, the half-life of an electron is calculated as $\tau = 318$ years for a given trap depth of $E = 1.28$ eV and frequency factor $s = 10^{12}\ s^{-1}$ at room temperature ($T = 20$ °C) by means of this equation. According to this equation, the half-lives of electrons in deep traps have been calculated to be hundreds or even thousands of years. If the temperature of material is increased, the half-life of electron is decreased for given trapping parameters. However, some of experimental studies have shown that the electrons caught in the traps were released in shorter time than one would expect according to the Eq. (1) [7–12] and some materials exhibit an unexpected fading effect even if the materials are held at temperatures well below that of the peak temperature of TL glow peak. This phenomenon is known as the anomalous fading effect.

Anomalous fading was first reported by Bull and Garlick [8]. Later, Hoogenstraaten [9], Schulman et al. [10], Wintle [11,12], Kieffer et al. [13], Bailiff et al. [14] and Spooner [15,16] reported similar mechanisms. Visocekas et al. [17] reported for a mineral that the fading rate had been measured and had shown to follow a temperature independent, logarithmic decay law. According to Visocekas [17], the tunneling recombination mechanism appears to be more prospective than the others among all possible mechanisms. Visocekas et al. [18,19] came up with an explanation for both afterglow and anomalous fading using quantum mechanical tunneling effect. Templer [20,21] reported that above room temperature, localized transitions are responsible for the anomalous fading whereas tunneling predominates at lower temperatures. Visocekas et al. [22] studied the tunneling effects leading to anomalous fading. Wood et al. [23] reported that anomalous fading mechanism had been observed in the absorption spectra of aluminum oxide.

Tyler and McKeever [24] reported that the anomalous decay in a material is more precisely described by the localized transition model of Templer [20–21] rather than by quantum mechanical tunneling.

On the other hand, Chen and Hag-Yahya [7] and Chen et al. [5] discussed the possibility that, in fact, anomalous fading may be in some instances just a normal fading in disguise. The idea is that the visible TL peak may look significantly narrower than anticipated with the given activation energy (E) and the frequency factor (s) of

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the peak due to the presence of non-radiative centers. It is important to point out that those electrons, which are thermally released from traps are then captured by radiative and non-radiative centers. Under such circumstances, it is possible to obtain higher activation energy values compared to real values using methods such as curve fitting or peak shape methods. Results obtained via these methods demonstrated that the apparent trap life-time values could be in orders of magnitude higher than the real values. Thus, when one expects a longer life-time due to the calculated parameters may in fact observe a shorter decay life-time, which is referred to as anomalous fading.

This fading is known as loss of charge carriers from trap levels via thermal or optical mechanisms. On the other hand, the anomalous fading is known as loss of charge carriers from thermally stable trap levels via athermal mechanism, i.e. by means of quantum mechanical tunneling effect. Anomalous fading may be due to many factors such as light, temperature or humidity. Several models have been proposed to explain the reasons behind anomalous fading. However, the quantum mechanical tunneling model seems to be the most probable mechanism when the anomalous fading is temperature independent.

According to this model, if the trap energy level and recombination centers are spatially located close to each other, the wave functions of charge carriers in the traps can be superposed. In such a case, charge carriers can move through traps and recombination centers via tunneling mechanism. The possible recombination of the charge carriers before reaching high delocalized energy levels is a crucial case, which has been observed for many thermoluminescence materials [8–14]. The comparison of the potential energy of electrons caught in traps and the holes in recombination centers as a function of the distance is shown in Fig. 1. As seen in the figure, an electron at distance r_1 is placed at the bottom of a potential barrier with depth E_1.

The tunneling occurs when the electron overcomes the potential barrier and moves to the recombination center. The probability of an electron to move between a trap and a recombination center pair separated with a distance r via tunneling is given by Eq. (2) [2] and luminescence intensity is given by Eq. (3) [25];

$$P(r) = P_0 \exp\left[-\frac{r}{a}\right] = P_0 \exp[-\alpha r] \tag{2}$$

$$I_{TL}(t) = -P(r) n_0 \exp[-P(r)t] \tag{3}$$

where P_0 is the frequency factor, a is a constant (roughly assumed to be the Bohr radius for the electron), n_o is the initial density of trapped charge and t is the time. The parameter α can be given by the following Eq. (4) [2,25]:

$$\alpha = 2\frac{\sqrt{(2m^*E_1)}}{\hbar} \tag{4}$$

where m^* is the effective mass of electrons, h is the Planck constant and $\hbar = h/2\pi$. As a result, the probability of an electron to move between a trap and a recombination center pair via tunneling decreases over time once the irradiation is stopped. This in fact appears as TL signal loss (fading) in the readout phase.

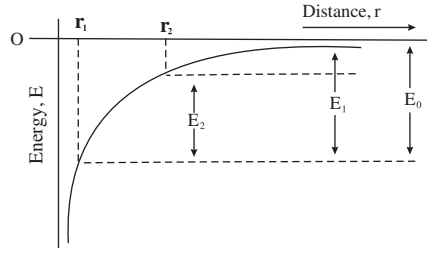

Fig. 1. Tunnelling mechanism with energy levels [6].

2. Experimental studies

In order to investigate the fading characteristics of all peaks in the glow curves of alumina samples obtained by Seydişehir in Turkey, the following experimental procedures were conducted.

The inorganic phases within the samples were first isolated from the samples and sieved to obtain a grain size between 45 and 63 μm. Before the thermoluminescence analysis, samples were annealed at 600 °C for 15 mins to erase any residual information before the subsequent irradiation. All annealing treatments were carried out with a specially designed microprocessor controlled electrical oven, which is able to control the temperature to within ±1 °C. The powder was spread on stainless steel disks, about 20 mg on each one. Sample was irradiated at room temperature using the beta rays from a calibrated ^{90}Sr–^{90}Y source. The typical strength of the source is about 2.4 Gy/min. The samples were exposed by β-ray during 2 min in each experiment. After first time irradiation, the glow curve of the sample was recorded without storing the samples. The time duration between irradiation and first TL reading was always kept constant at about 1 min. After the glow curve measurement, the samples were re-annealed at 600 °C for 15 min and irradiated by β-ray during 2 min and then they were stored in dark conditions and dry environment at room temperature, between 25 and 30 °C, over desired periods (6 h, 1, 7, 14, 30 and 60 days). The glow curves of irradiated sample were measured at a linear heating rate of 1 °C/s between room temperature and 400 °C using a Harshaw QS 3500 manual type reader, which has an S-11 response photomultiplier tube and that is interfaced to a PC where the signals were studied and analyzed. A standard clean glass filter was always put in the reader between sample and photomultiplier tube. This filter permits the light whose wavelength is between ≈250 and ≈1000 nm to pass through the filter and so, unwanted infrared light that is emitted from the heater is eradicated. Each sample was readout twice during each experimental measurement. The second readout was considered to be the background of the reader and sample; this was subtracted from the first one and all of the analyses have been carried out after the subtraction. Finally, the TL glow curves were again recorded at the end of desired period. All the recorded glow curves were analyzed using a glow curve analyzing program, which was developed at the Reactor Institute at Delft, The Netherlands. [26].

3. Experimental results

Before the investigation of fading characteristics of glow peaks in the glow curve of Seydişehir alumina, one of the glow curves of this material was analyzed by computerized glow curve deconvolution program. A typical analyzed glow curve of this material is shown in Fig. 2. As seen, the Seydişehir alumina has 4 glow peaks between 100 and 400 °C. They are situated at 117 ± 1.8 °C (P_1), 175 ± 1.8 °C (P_2), 196.6 ± 1.8 °C (P_3) and 326 ± 1.8 °C (P_4). The sum of peaks 2 and 3 can be referred to as the main peak.

Many dosimetric characteristics of TL materials mainly depend on kinetic parameters quantitatively describing the trapping-emitting centers responsible for the TL emission. Thus, the determination of the kinetic parameters is an active area of research. For example, the simultaneous estimation of the dose rate and the time elapsed since exposure are closely related to the position of the trapping levels within the band gap, and therefore it is necessary to have a good knowledge of these parameters. There are various methods for evaluating the trapping parameters from TL glow curves such as initial rise, additive dose, peak shape, various heating rate, T_m–T_s and CGCD [1,4]. In this study, the trapping parameters of all glow peaks of Seydişehir aluminas

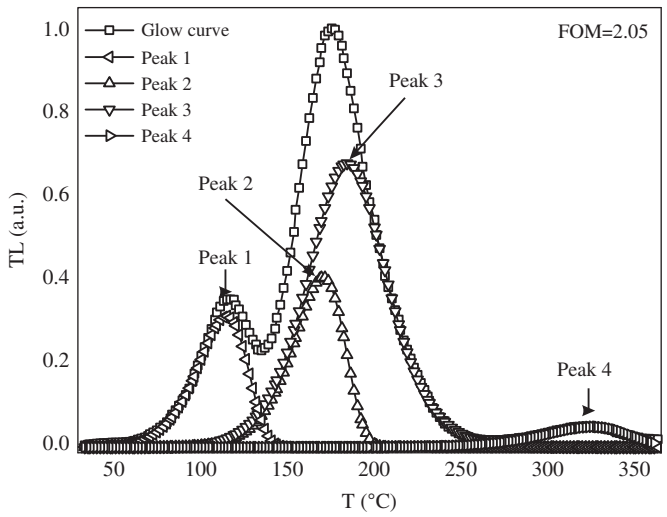

Fig. 2. An analyzed glow curve of Seydişehir alumina at a heating rate of 1 °C/s following β-ray exposure at room temperature for 2 min (≈ 4.8 Gy).

Table 1
TL parameters of these peaks [1].

Peak	T_m (°C)	E (eV)	ln [s] (s^{-1})	τ (day) Eq. (1)
1	117.0 ± 1.8	0.85	22.2	1
2	175.0 ± 1.8	1.28	26.5	360017
3	196.6 ± 1.8	0.88	18.4	158
4	326.0 ± 1.8	1.75	28.3	7.4×10^{12}

have been studied using initial rise, additive dose, peak shape, various heating rate, T_m–T_s and CGCD methods. As a result, the obtained kinetic parameters were given in Table 1 [1]. The parameters given in Table 1 are the average values of the results of all the calculation methods mentioned previously and the values given in last column are calculated using E and s values from Table 1 and Eq. (1) at room temperature.

The stability of the stored signal at RT is an important factor in many applications such as archeological and geological dating, personal and environmental dosimetry. Any appreciable decay in the stored signal will invalidate the relationship between TL emitted and the radiation exposure that may have been delivered some considerable time before readout. The extent of TL signal decay over long periods is difficult if not impossible to measure directly, particularly in archeological applications. Some of the measured glow curves of Seydişehir alumina at the end of the planned storage periods are shown in Fig. 3. As seen from this figure, the peak intensity and area of glow peaks P_1, P_2, P_3 and P_4 are quickly decreased while a new peak, which is observed at 378 ± 2 °C, is highly increased from storage periods at RT. As seen, after the storage at RT for 1 month, it can be assumed that P_1 was removed from the glow curves. In addition to this, the main dosimetric glow peak (P_2+P_3) was faded ($12\% \pm 2$), ($35\% \pm 1$), ($45\% \pm 2$) at the end of 6 h, 1 and 7 days storage periods, respectively. After 14, 21, 30 and 60 days, the amount signal losses of main glow peak were obtained as ($50\% \pm 2$), ($53\% \pm 3$), ($56\% \pm 3$) and ($65\% \pm 3$), respectively. On the other hand, the intensity of new peak at around 378 ± 2 °C is continuously increased with increasing storage time (see Fig. 3). It was observed that the increase in the intensity of this peak is approximately equal to $125\% \pm 5$, $2150\% \pm 50$ at the end of 6 h and 30 days, respectively. The normalized relative responses of analyzed glow peaks are shown in Fig. 4.

It can be seen from Fig. 4, while the fading level of peak 2 decreases the fading level of peak 3 increases and vice versa.

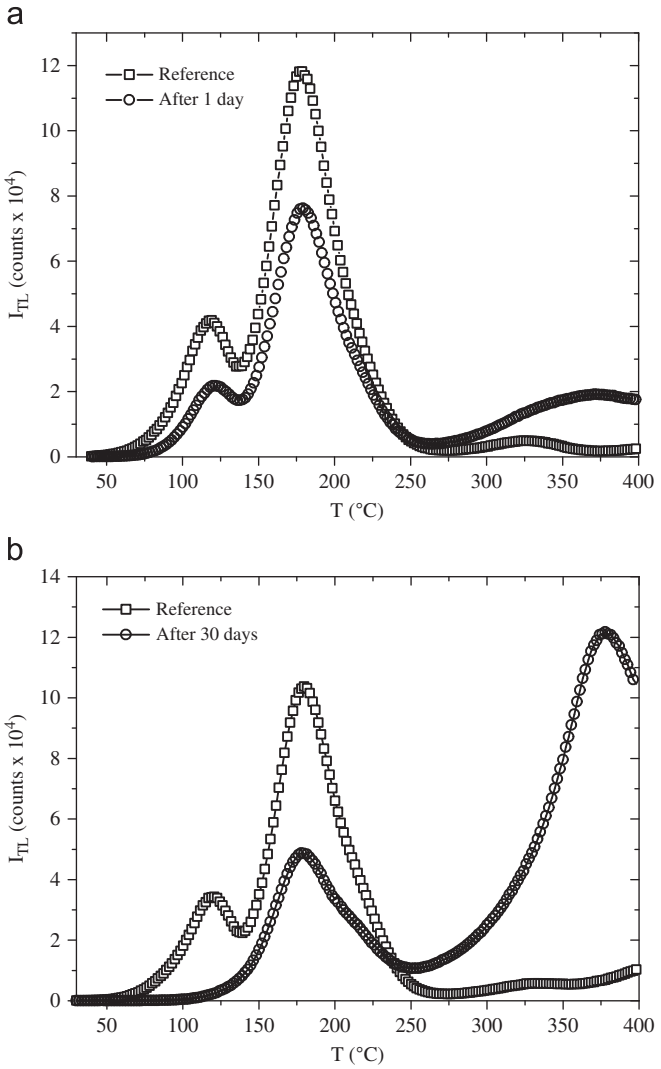

Fig. 3. (a) Some of the selected glow curves of Seydişehir alumina recorded after different storage periods at RT in the dark room and (b) some of the selected glow curves of Seydişehir alumina recorded after different storage periods at RT in the dark room.

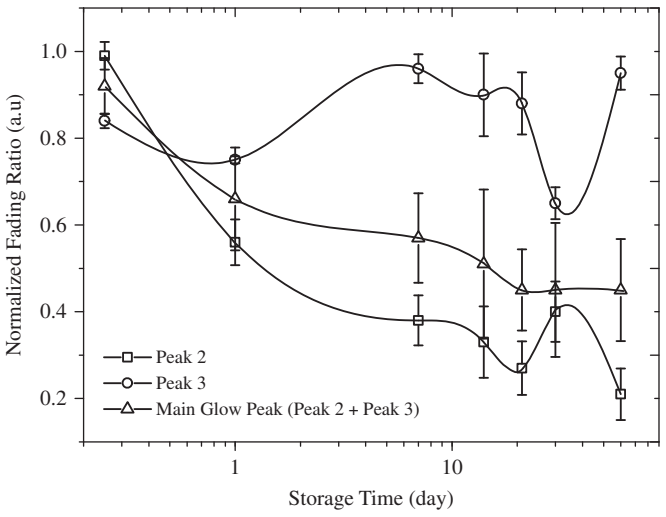

Fig. 4. The fading evaluation of the deconvoluted peaks of Seydişehir alumina at RT in the dark room.

This behavior can be interpreted that an interactive interaction between peaks 2 and 3 is present. Thus, their fading ratios differ. However the main glow peak (P_2+P_3) continuously fades with time. This effect can also be explained via electron band diagram, which was proposed for Seydişehir alumina, as seen in Fig. 5. In the given figure, the transitions 1, 2, 4 and 5 represent the thermal excitation mechanisms, which occurred during heating stage and 3 represents the tunneling mechanisms.

In the given study, a set of differential equations, which are representing the charge carrier transitions in the electron band diagram of Seydişehir alumina in Fig. 5 is also derived. Numerical analyses of these equations were performed via computer software with the initial conditions given in Table 1. It is observed that the calculated and experimental glow curves are consistent as seen in Fig. 6 (FOM=0.12). It was observed that the calculated and experimental glow curves are very consistent with each other.

Half-lives of the charge carriers in traps were calculated using Eq. (1) with the data from Table 1. Then, the surviving ratios of the charge carriers in each trap were calculated by taking into consideration their half-lives by neglecting the anomalous fading effect. In addition , the peak heights of peaks 2 and peak 3 were determined via CGCD at the end of every storage time and these results are presented in Fig. 7. It was observed that the normal fading ratio of peak 2 is very low so that it can be neglected while

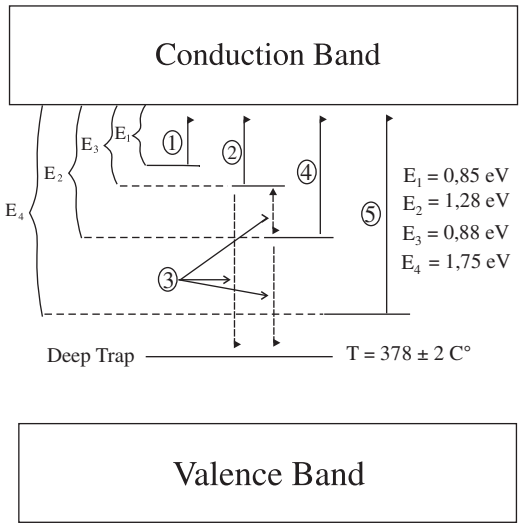

Fig. 5. An electron-band diagram proposed for Seydişehir alumina.

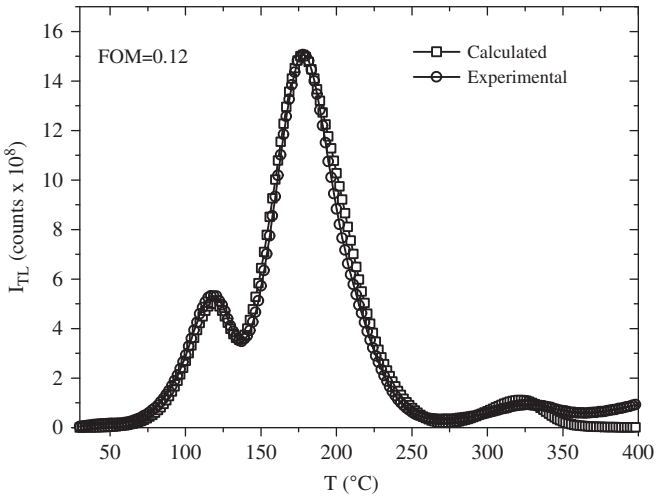

Fig. 6. Experimental and numerically generated glow curves of Seydişehir alumina.

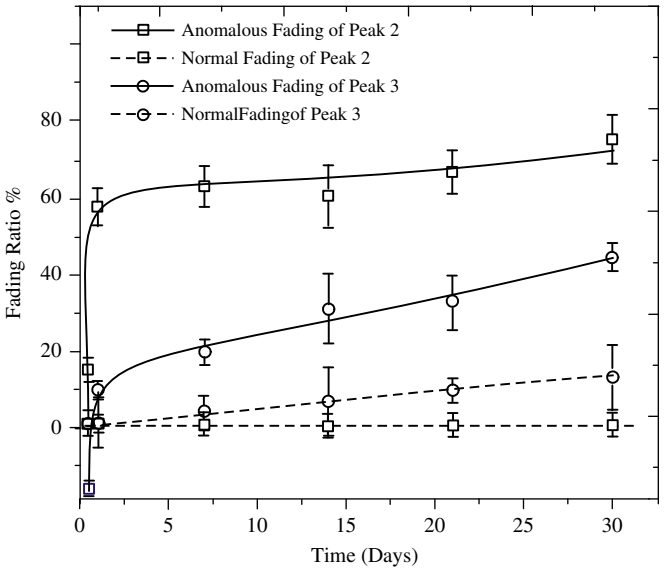

Fig. 7. Normal and anomalous fading ratios of peak 2 (square) and peak 3 (circle).

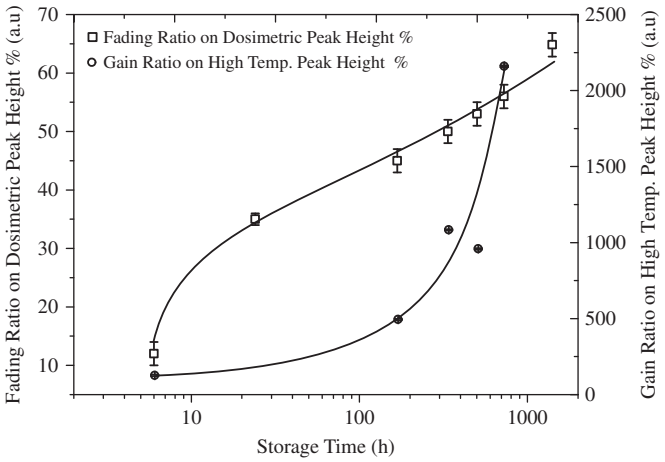

Fig. 8. Fading ratio on dosimetric peak height and gain ratio on high temperature. peak height after different storage period.

its anomalous fading ratio is very high and increases minus exponentially (see Fig. 7). According to Eq. (3), the tunneling probability increases minus exponentially with increasing storage time. In Fig. 7, it can be seen such characteristics of tunnel mechanism has caused high level anomalous fading of peak 2. Besides, peak 3 shows the same behavior for normal and anomalous fading ratios with the anomalous fading ratio being higher than the normal fading ratio.

Moreover, simultaneously with the signal loss of the dosimetric glow peak, it was observed that the density of the peak at high temperature region (378 ± 2 °C) rapidly increased (see Fig. 8).

4. Discussion

The experimental results point out that even if the samples were kept in a dry environment and no direct contact to light during storage period, the glow peaks (P_1–P_4) of Seydişehir alumina have very high levels of fading. These fading levels are so high that they cannot be explained by thermal fading. Moreover, it was observed that the intensity of the glow peak at high temperature regions above 350 °C is continuously increased with time along with the

signal losses of the glow peaks below 250 °C. At the same time, the amounts of fading of peaks 2 and 3 were irregularly altered with time, i.e. one of them is increased the other decreased or vice versa. This means that some of the electrons present in trap 2 moved into trap 3 or from trap 3 to 2 via tunneling mechanism. As a result of this observation, it was interpreted that the fading mechanism of Seydişehir alumina cannot be explained by regular fading mechanism, it can only be explained by anomalous fading mechanism.

Finally, we have concluded that the electrons generating the dosimetric peak move into each others' and deep electron traps via tunneling mechanisms.

References

[1] E. Uzun, Ph.D. Thesis, İstanbul, 2008.
[2] R. Chen, S.W.S. McKeever, Theory of Thermoluminescence and Related Phenomena, Word Scientific, Singapore, 1997.
[3] R. Chen, D.J. Lockwood, Journal of the Electrochemical Society 149 (9) (2002) 69.
[4] C. Furetta, Handbook of Thermoluminescence, Word Scientific, New Jersey, 2003.
[5] R. Chen, P.L. Leung, M.J. Stokes, Radiation Measurements 32 (2000) 505.
[6] S.W.S. Mckeever, R. Chen, Radiation Measurements 27 (5/6) (1997) 625.
[7] R. Chen, A. Hag-Yahya, Radiation Measurements 27 (2) (1997) 205.
[8] C. Bull, G.F.J. Garlick, Proceedings of the Physical Society of London 63 (1950) 1283–1291.
[9] W. Hoogenstraaten, Philips Research Report 13 (1958) 515.
[10] J.H. Schulman, R.J. Ginther, S.G. Gorbics, A.E. Nash, E.J. West, F.H. Attix, Applied Radiation and Isotopes 20 (1969) 523.
[11] A.G. Wintle, Nature 245 (1973) 143.
[12] A.G. Wintle, Journal of Luminescence 15 (4) (1977) 385.
[13] F. Kieffer, C. Meyer, J. Rigaut, Chemical Physics Letters 11 (1971) 359.
[14] I.K. Bailiff, S.G.E. Bowman, S.F. Mobbs, M.J. Aitken, Journal of Electrostatics 3 (1–3) (1977) 269.
[15] N.A. Spooner, Quaternary Science Reviews 11 (1–2) (1992) 139.
[16] N.A. Spooner, Radiation Measurements 23 (2-3) (1994) 625.
[17] R. Visocekas, Nuclear Tracks and Radiation Measurements 10 (4–6) (1982) 521.
[18] R. Visocekas, M. Ouchene, B. Gallois, Nuclear Instruments and Methods in Physics Research 214 (2–3) (1983) 553.
[19] R Visocekas, International Journal of Radiation Applications and Instrumentation. Part D. Nuclear Tracks and Radiation Measurements 14 (1–2) (1988) 163.
[20] R.H. Templer, Nuclear Tracks and Radiation Measurements 10 (1985) 531.
[21] R.H. Templer, Radiation. Protection. Dosimetry 17 (1986) 493.
[22] R Visocekas, V. Tale, A. Zink, N.A. Spooner, I. Tale, Radiation. Protection. Dosimetry 66 (1996) 391.
[23] R.A. Wood, P.D. Townsend, G.P. Pells, M.J. Murphy, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 46 (1–4) (1990) 189.
[24] S. Tyler, S.W.S. McKeever, Nuclear Tracks and Radiation .Measurements. 14 (1988) 149.
[25] S.W.S. Mckeever, Thermoluminescence of Solids, first ed., Cambridge University Press, Cambridge, 1985.
[26] A.J.J. Bos, J.M. Piters, J.M. Gomez Ros, A. Delgado, IRI-CIEMAT Report 131-93-005, IRI Delft, 1993.