Dependence of the anomalous fading of the TL and blue-OSL of fluorapatite on the occupancy of the tunnelling recombination sites

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Abstract

The anomalous fading (AF) of thermoluminescence (TL) and optically stimulated luminescence (OSL) signals in Durango apatite is attributed to tunnelling effects. Electrons from the TL and OSL traps in this material are transferred, via a tunnelling effect, to the recombination sites. The availability of recombination sites for tunnelled electrons is of major importance for the degree of AF rate observed in this material. It is expected that a variation of the number of the electron recombination sites will be reflected in the experimentally measured AF rate. In the present work an investigation of the recombination sites for the tunnelled electrons is attempted by studying the AF effect using a special technique, in which the anomalously faded TL (OSL) is replaced by an equal amount of TL (OSL) induced by a beta dose.

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1. Introduction

Anomalous fading (AF) is the term adopted for the rapid decay at room temperature of the high-temperature thermoluminescence (TL) glow-peaks signal, contrary to the expected stability predicted by the basic TL kinetic models. Several models have been proposed to explain the effect [1,2]. In these cases where the AF is temperature independent the quantum mechanical tunnelling [3,4] seems to be the most probable mechanism. For the cases where the AF is temperature dependent the suggested models are thermally assisted tunnelling [4], localized transitions [5,6] and a model which considers AF as normal fading in disguise [7].

The AF factor \( r \) is unique for each glow-peak of a glow-curve and shows a remarkable resistance to variation even when extreme external conditions are applied to the material. Kitis et al. [8] studied the AF rate of Durango apatite as a function of grain size, annealing temperature, pre-dose and irradiation temperature and had found that the \( r \) factor is not seriously influenced at all by all these external parameters with the exception of one case. The AF was found to increase after 1 h annealing at 1000 °C. Polymeris et al. [9] found that both TL sensitivity and the AF factor of the main TL glow-peak of Durango apatite shows a remarkable stability over many irradiation-storage time-TL readout cycles. The same was also found for the fast component of the optically stimulated luminescence (OSL) decay curve, whereas the slow component was sensitized.

The aim of the present work is to apply some mild experimental procedure, which can lead to variations of the measured AF factor \( r \). The term measured AF is adopted in order to distinguish our experimental results from the intrinsic AF which is due to tunnelling effects only.

In the case of AF, trapped electrons escape via tunnelling from their traps and recombine in a recombination site of
an unknown nature. The question arises whether it is possible to alter the number of these unknown recombination sites and subsequently the AF factor $r$. An experimental technique which could achieve this is described below.

**Step 1:** Give a test dose to a sample and measure the TL and OSL immediately after the end of irradiation. In this way the zero storage time of TL or OSL signal is obtained, as well as, the calibration factor in terms of TL or OSL per unit dose.

**Step 2:** Give the same dose to the sample and measure the TL and OSL after a storage time $t$ at dark conditions. In this way the AF factor $r$ is obtained. Find the difference of the TL (OSL) between the zero storage time (step 1) and storage time $t$ (step 2). Find the dose corresponding to this difference using the calibration factor obtained in step 1.

**Step 3:** Use the dose obtained in step 2 to irradiate the sample and (i) measure the TL or OSL signal immediately after the irradiation in order to obtain (or not) a TL (OSL) signal equal to that corresponding the zero storage time, (ii) measure the signal after its storage at dark conditions for time $t$ equal to that used in step 2, in order to obtain the new AF factor.

During the AF of the sample in step 2, it is expected that a number of recombination sites has been removed. Therefore, after the irradiation of the faded sample by a dose corresponding to the TL (OSL) lost by AF and its subsequent storage for the same time interval, the expected anomalous loss of TL (OSL) will be less, due to the lower number of available recombination sites. The detailed experimental procedure is described in the corresponding section below.

2. Material and apparatus

The study was performed on Durango apatite, a type of apatite which is known to exhibit strong AF of its TL signal [8]. The sample was initially crushed, and grains with dimensions 2–10 μm were selected and deposited on aluminum disks of 1 cm² area using the Zimmerman method [10]. The grains were annealed at 500 °C for 1 h.

The measurements were performed using the RISO TL/OSL reader (model TL/OSL-DA-15) equipped with a high-power blue LED light source, an infrared solid state laser and a $^{90}\text{Sr}/^{90}\text{Y}$ β-ray source delivering 0.085 Gy/s for in situ irradiation.

The TL measurements were performed using a combination of a Pilkington HA-3 heat absorbing filter and a Corning 7-59 blue filter, using a heating rate of 5 °C/s and a maximum heat temperature of 500 °C. The OSL measurements were performed for 100 s using a Hoya U-340 filter at room temperature. The power level was software controlled and set at 90% for blue LED measurements.

According to the above settings of the TL/OSL reader, the AF of TL and OSL was studied in separate experiments following the same protocol, which is described in the following section. The protocol was applied on a single aliquot (SA) since, as was shown in detail by Polymeris et al. [9], the TL and OSL sensitivity of Durango apatite shows a remarkable stability over more than 10 successive irradiation-readout cycles.

3. Experimental results

3.1. AF versus number of recombination sites for tunnelled electrons

The behavior of the AF as a function of the number of tunnelled electron recombination sites was investigated by using several successive cycles, each one including an incremental number of irradiation-storage-measurement steps, as shown in Table 1.

In the first cycle (A) the sample is irradiated with a test dose of 15.3 Gy (step 1) then the TL/OSL is measured immediately after the end of irradiation (step 2). This procedure yields: (i) zero storage time sensitivity, which is used as a reference value to normalize all other measurements and (ii) a calibration factor for the TL (OSL) signal per unit dose.

In the second cycle (B) the sample is irradiated with the test dose (step 1), stored for a time interval $t$ (step 2), and

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**Table 1**

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$S =$ step, $I =$ irradiation, $M =$ measurement, $St =$ storage.
then measured (step 3). This procedure yields the measured AF factor \( r_1 \), which corresponds to the time interval \( t \). The dose \( D_1 \) that corresponds to the TL (OSL) lost during the time interval \( t \), can be estimated by using the calibration factor obtained in the first cycle.

In the third cycle (C) steps 1 and 2 of cycle (B) are repeated, then the sample is irradiated with dose \( D_2 \) that was estimated in the previous cycle (step 3) and measured immediately after the irradiation (step 4). In principle, the recorded TL (OSL) signal should be equal to the reference sensitivity obtained in cycle (A).

In the fourth cycle (D) steps 1–3 of the cycle (C) are repeated, then the sample is stored again for the same time interval \( t \) (step 4) and finally measured (step 5). This procedure yields the new AF factor \( r_2 \), which reflects any changes induced by the varying number of available recombination sites. The new dose \( D_2 \) that corresponds to the loss of the TL (OSL) is estimated as in the second cycle (B).

The above incremental procedures are continued for six more cycles (E, F, G, H, I and J) that follow the same principles, i.e. in the fifth cycle (E) steps 1–4 of the cycle D are repeated, then the sample is irradiated with dose \( D_2 \) that was estimated in the previous cycle (step 5) and measured immediately after irradiation (step 6) and so forth.

The entire measurement protocol is described symbolically in Table 1. It should be noted that the same protocol was used for both the TL and OSL measurements.

The complete experimental protocol consists of five cycles similar to those described above. In brief, row 1 yields the normalization factor. The ratio of rows 3, 5, 7 and 9 over row 1 in Table 1 gives the recycling ratio, which must be as close as possible to unity. Row 2 gives the first AF factor before any changes occur to the recombination sites, whereas rows 4, 6, 8 and 10 give the AF factors after the attempted change of the number of the recombination sites in rows 3, 5, 7, and 9.

The results from each cycle can be summarized briefly as follows:

1. Cycle A yields the zero storage time sensitivity which is used as a normalization factor.
2. Cycles C, E, G, and I yield the recycling ratio (ratio of the glow-curve integral of the specific cycle over cycle A), which should be as close to unity as possible.
3. Cycle B yields the original AF factor before any alterations in the number of the recombination sites.
4. Cycles D, F, H, and J yield the AF factors after the possible alterations in the number of the recombination sites induced in cycles C, E, G and I.
5. After the end of each TL and OSL cycle the sample was annealed by performing a TL readout up to 500 °C.
6. After the end of the last cycle and the TL readout up to 500 °C, the sample was irradiated by the first test dose and was stored for a time interval equal to that of the first cycle. The AF factor obtained in this way is compared with the AF factor of the first cycle. This final action is performed in order to test whether the readout up to 500 °C considered as an annealing can restore the AF factor to its original values (of the first cycle).

The TL (OSL) signal is the remnant TL (OSL) i.e. the TL (OSL) remaining after the storage of the sample at room temperature for various time intervals from the end of irradiation. The remnant TL (OSL) is defined by the parameter \( r \), which is the ratio of the TL (OSL) at time \( t \) over to the initial TL (OSL) at time 0. In the case of the tunneling model for the AF, and when the time \( t \) is much longer than the irradiation time, \( t_i (t > t_i) \) then the remnant TL (OSL) ratio \( r \) is described by an equation of the form [1,3,4,11].

\[
r = A - K \cdot \ln \left( \frac{t}{t_0} \right),
\]

where \( A = 1 \). However, for fitting needs, \( A \) can be considered a free parameter varying around 1.

The fading rate in terms of percentage per decade \( g \), [12] is related to \( K \), [2,13] by:

\[
g = 230.2 \cdot K.
\]

The TL glow-curve of Durango apatite annealed at 500 °C for 1 h and measured with a heating rate of 5 °C/s, consists of a low intensity glow-peak at about 170 °C, a very high intensity glow-peak at about 310 °C and a high-temperature region above 400 °C. This latter high temperature peak is the residual of glow-peaks above 500 °C, not erased by the annealing of 500 °C for 1 h. By performing a series of 12 successive irradiation-readout cycles it was found that the sensitivity of the main peak (310 °C) remains stable within less than 2% [9]. Further details concerning the deconvolution of the glow-curves using second order kinetics were given by Polymeris et al. [9].

The results related to the TL integral between 170 and 380 °C of the main TL glow-peak of Durango apatite are shown in Fig. 1. The triangular points are the experimental values of the recycling ratio while the dash line represents a recycling ratio of unity. As can be seen from the figure, the initial fading factor (provided by cycle B), is substantially decreased (approaching unity) as a function of successive cycles of AF-regenerating by irradiation the faded TL. Curve (a) corresponds to storage time of 1 h, curve (b) to storage time of 2 h and curve (c) to storage time of 12 h. The higher the storage time the faster the recovery of AF. The reason is that during longer storage times, more TL has faded, so that more recombination sites for tunnelled electrons have been removed. The errors which are not shown on the figure for the sake of clarity, were within less than 3%. After the end of the last cycle and the TL readout up to 500 °C, the sample was irradiated by the first test dose and was stored for a time interval equal to that of the first cycle. The AF factors obtained were exactly equal to those of the first cycle for all cases (a)–(c). This final
measurement shows that the readout up to 500°C can restore the AF factor to its original values.

All OSL measurements were performed at room temperature in order to avoid any thermal effect on the OSL traps. Preheat was not necessary, since the lower temperature glow-peak of the TL glow-curve is around 200°C and has very low intensity compared to the higher temperature segment of the glow-curve. The OSL signal was measured using two different methods: (i) the single aliquot regenerative (SAR) dose protocol[14], i.e. integral of the first second minus the mean of the last 5 s, which are considered to be background. This method was also used during the OSL measurements in order to evaluate the calibration factor, OSL per unit dose (see the experimental protocol above). (ii) The second method involved the transformation of the OSL decay curves into a pseudo-linear modulated (pseudo-LM) one, using the transformation suggested by Bulur[15]. Once the OSL decay curves were transformed into pseudo-LM curves, they were analyzed into their individual components using the general order kinetics equation given by [9]:

$$I(u) = \frac{I_m}{u_m} \cdot u \cdot \left[ \frac{\beta - 1}{2\beta} \cdot \frac{u^2}{u_m^2} + \frac{\beta + 1}{2\beta} \right]^{\beta/(1-\beta)}$$

where $t$ is the time, $P$ is the total illumination time, $\beta$ is the kinetic order, $u = \sqrt{2tP}$ (or $t = u^2/2P$), $u_m$ is the value of $u$ at $t_m$ and $I_m$ the maximum intensity at $t_m$.

The fitting to pseudo-LM OSL decay curves was performed with the MINUIT program [16], whereas the goodness of fit was tested using the figure of merit (FOM) of Balian and Eddy [17] given by

$$FOM = \sum_i \frac{|Y_{\text{Exper}} - Y_{\text{Fit}}|}{A}$$

where $Y_{\text{Exper}}$ is the experimental glow-curve, $Y_{\text{Fit}}$ is the fitted glow-curve and $A$ is the area of the fitted glow-curve. The FOM values obtained were in all cases between 0.6% and 0.9%, which must be considered as exceptionally good. Further details concerning the pseudo-LM OSL curves and their deconvolution using second order kinetics are given by Polymeris et al. [9].

Fig. 2 shows the results for the fast component of the OSL decay curve of Durango apatite. The behavior is similar to the one observed for TL. Curves a, b, and c are obtained for storage time of 10 min and curve (d) for a storage time of 60 min. The curves a, b and c, correspond to three samples with different radiation and thermal history. Sample (a) is a virgin sample (never used before), sample (b) is a ‘lightly’ used sample, and sample (c) is a ‘heavily’ used sample. Fig. 3 shows similar results obtained for the slow OSL component. The errors, not noticed on the figure for the sake of clarity, were within less than 3%. As in the case of the TL measurements, after the end of the last cycle and the TL readout up to 500°C the sample was irradiated by the first test dose and was stored for a time interval equal to that of the first cycle. The AF factors obtained were exactly equal to those of the first cycle for all cases (a)–(d). This final measurement shows that the readout up to 500°C considered as an annealing can restore the AF factor to its original value.
number of trap-recombination site pairs located at longer distances will be increased. The combination of these effects should be reflected also in the measured AF factor.

Of course the real situation is much more complicated since, for example, all the TL glow-peaks of Durango apatite exhibit AF, and not only the main peak considered here [9]. However, the simultaneous study of all glow-peaks is limited by the fact that the experimental procedure used here is strongly dependent upon the exact evaluation of the calibration factor on which the successive irradiations are based. As a result of this experimental limitation, only the main peak was considered in the present study. However, despite the complexity of the situation, the simple explanations and the numerical calculations given below are quite plausible, and the results in close agreement with experiment.

The experimental results presented in Figs. 1–3 can be numerically reproduced by taking into account the percentage of the tunnelling recombination sites which are filled at every cycle. Let us take for example the case of storage time of 1 h shown in Fig. 1, curve (a). After a storage time of 1 h the remnant TL is \( r = 0.75 \) evaluated by Eq. (1) using \( K = 0.089 \) and \( t_0 = 0.038 \) obtained in a previous work by Polymeris et al. [9]. This means that 29% of the initial number of electron-positive charge pairs have decayed after 1 h, and \(~71\%\) of them remain in material.

In the next step of irradiation a re-filling dose is given to the sample to replace the 29% that was lost during the first hour, so that again 100% of the pairs exist in the sample. In our mathematical description this means that 100% of the initial number of pairs will decay for a total time of \( t_1 = 2\) h, from the start of the whole experiment, while the 29% of the pairs will decay only for \( t_2 = 1\) h. Thus the total remnant TL after the total time of 2 h of the experiment is given by the sum of the two remnant TLs:

\[ r_{\text{total}} = r_1 + r_2, \]  
where,

\[ r_1 = 1 - K \cdot \ln \left( \frac{t_1}{t_0} \right), \]  
and

\[ r_2 = 1 - K \cdot \ln \left( \frac{t_2}{t_0} \right). \]

By inserting the values of \( K = 0.089, t_0 = 0.038, t_1 = 2, \) and \( t_2 = 1\) h, then Eq. (5) becomes

\[ r_{\text{total}} = \left[ 1 - 0.089 \cdot \ln \left( \frac{2}{0.038} \right) \right] + 0.29 \cdot \left[ 1 - 0.089 \cdot \ln \left( \frac{1}{0.038} \right) \right] = 0.85. \]  

This value is in agreement with the experimental data for cycle 2 in Fig. 1. This value of \( r = 0.85 \) means that during the next cycle 3, 15% of the original number of pairs will decay for 1 h, while 29% of the pairs decay for 2 h, and

\[ t_1 = 2, \quad t_2 = 1, \quad t_0 = 0.038, \quad K = 0.089. \]

Fig. 3. The anomalous fading factor, of the second component of the BSL decay curve, resulting from the refilling procedure described in Table 1 as a function of the storage time-filling cycle. Curves (a, b, c) correspond to storage time of 10 min and curve (d) to storage time for 60 min. The experimental points around the dash line represent the values of the recycling ratio, which must close to 1. The open symbols represent the calculated values as described in the text.

4. Discussion

The TL/OSL properties of various materials are due to effects which are taking place either during the irradiation-absorption stage, or during the readout-recombination stage, or during both stages. In the present work the readout conditions of both TL and OSL are kept stable and exactly the same for all measurements, so that the experimentally measured values of the AF factor \( r \) are believed to be due to the same recombination stage effect. On the other hand, the tunnelling effect is a special case of a recombination effect taking place at a stable room temperature during storage. The irradiation of a sample, which has already partially faded anomalously, leads to the following situation within the sample. Some of the tunnelling recombination sites have been removed (however, one can suppose that a large amount of them should be available). Since the doses used in the present work are much lower than the saturation dose, (which is greater than \( 10^3\) Gy for TL and greater than \( 10^2\) Gy for OSL [9]), there are many empty electron traps, which can trap electrons created by the additional irradiation. It must be noted that the electrons in the conduction band cannot distinguish between a trap which was always vacant and a trap which was filled and then emptied. Taking into account that this procedure can be repeated for many cycles one can argue as follows: (I) groups of filled traps are formed, each corresponding to a different storage time. (II) The tunnelling probability (which is related to the intrinsic AF rate) depends on the distance between the rap and the tunnelling recombination sites. During AF the closer spaced trap-recombination site pairs are annihilated first. Therefore, after many irradiation-storage cycles, the...
100% of them decay for $3\text{h}$. By repeating this type of calculations for cycle 3 one obtains the value

\[ r_{\text{total}} = \left[ 1 - 0.089 \cdot \ln\left( \frac{3}{0.038} \right) \right] + 0.29 \cdot \left[ 1 - 0.089 \cdot \ln\left( \frac{2}{0.038} \right) \right] + 0.15 \cdot \left[ 1 - 0.089 \cdot \ln\left( \frac{1}{0.038} \right) \right] = 0.90. \]  

(9)

This value is again in agreement with the experimental data for cycle 3 in Fig. 1. In a similar manner the values 0.93 and 0.94 are calculated for cycles 4 and 5, respectively. The results for all cycles and for all three curves (a)–(c) in Fig. 1 are represented by the open symbols shown in Fig. 1, where one can see the very close agreement between experimental data and those obtained from the above described calculations.

Good agreement of the calculations and the experimental data was also found for the cases of both fast and slow components of OSL and are shown as the open symbols in Figs. 2 and 3. The $K$ values, taken from [9] were 0.1232 and 0.1047 for fast and slow components, respectively, whereas the $t_0$ values were 0.183 and 0.2, respectively.

All the above described calculations can be finally described by the following equation:

\[ r_i = \sum_{i=1}^{n} \left( 1 - r_{i-1} \right) \left( 1 - K \cdot \ln\left( \frac{n - i + 1}{t_0} \right) \right) \]  

(10)

with $r_0 = 0$ corresponding to a situation where the TL (OSL) signal has faded completely.

5. Conclusions

In natural materials exhibiting AF there is a continuous competition process between trap filling during natural irradiation and trap emptying due to tunnelling recombination. Some of the possible factors influencing the degree by which the sample arrives to an equilibrium state are the natural irradiation rate, the tunnelling recombination cross-section and finally, the available number of tunnelled recombination sites, which are the competitors to the occupation of electron traps.

Since the natural dose rate is extremely low, it is rather impossible to simulate the natural situation in laboratory conditions. In this work we attempted to simulate the effect of the number of the competitor tunnelled recombination sites on the apparent AF factor $r$ of the sample. The results of our simulation should reflect some of the properties of the natural situation.

The results of the experiments in the present work are straightforward. The reduction of the number of recombination sites for tunnelled electrons leads to the reduction of the measured fading factor $r$ of the TL (OSL) signal, as shown in Figs. 1–3. Another important result is that the recovery of the AF factor disappears if the sample is heated for TL readout. If a readout take place, then the original value of the AF is obtained.

Both of these results, as well as the close agreement between our calculations and the experimental data, are consistent with the assumption that in a freshly irradiated sample the AF fading factor $r$ does not depend on the initial concentration of electron-hole pairs in the material. On the other hand, when the anomalously faded TL (OSL) is replaced by an additional beta dose, the sample will subsequently exhibit a reduced measured apparent fading factor $r$. This apparent lower AF factor is due to the existence of several groups of electron-hole pairs with different relative concentrations. Each one of these groups fades with the same fading rate $K$, but the total fading factor $r$ appears to be reduced.

References