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# Dose–response of thermoluminescence in natural kaolinite

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ABSTRACT

The thermal effect on the luminescence emission of a well-characterized natural kaolinite has been investigated by means of differential thermal analysis (DTA) and thermoluminescence (TL) to determine, respectively, the modifications of the material due to the thermal treatments up to 1000 °C and its potential use in the field of dating and retrospective dosimetry. The DTA detects water loss starting at 100–120 °C, a dehydroxylation process in the range of 400–500 °C and the transformation of kaolinite into metakaolinite at 570 °C. The dose dependence of the 400 nm TL intensity of kaolinite exhibits an excellent linearity in the range of 50 mGy to 8 Gy. In addition, the stability of the induced TL signal after six months of storage shows an initial rapid decay (ca. 60%) followed by a mild slope reaching the stability longer than six months. The tests of thermal stability at different temperatures allow us to speculate in a continuum of trap distribution with progressive changes in the glow curve shape, intensity and temperature position of the maximum peak. According to this thermal behavior, some physical parameters have been estimated using the initial rise method.

## 1. Introduction

Kaolinite ($Al_2Si_2O_5(OH)_4$), also known as china clay, is one of the most common clay minerals that is usually employed as raw material in the production of ceramics and porcelains, paper coatings, toothpaste or cosmetics, among others. They are often manufactured by heating of this material giving rise to dehydration and dehydroxylation processes that have been widely studied by means of differential thermal analysis and thermogravimetry (DTA-TG) [1] or thermal X-ray diffraction (TXRD) [2]. However, studies on the thermally stimulated luminescence (TSL or TL) emission of kaolinite were scarcely achieved before. To the best of our knowledge, only Guinea et al. [3], try to explain the different processes that take place during the thermal treatment of kaolinite and the influence in the blue thermoluminescence (TL) emission. Thus, the comparison between TL and electrical conductivity signal could explain the proton conductivity at pre-dehydration temperatures and could also indicate the presence of two different hydroxyl ions in the kaolinite structure: (a) $OH^-$ located within the six-member ring formed by $SiO_4$ tetrahedral sheet and (b) $OH^-$ array formed by the octahedral sheet. It is known that the original ordering of kaolinite structure disappears with the thermal heating along the *c*-axis, but is maintained along the *a* and *b* axes. The kaolinite lattice exhibits a typical T–O–T clay structure; it means a sheet of $SiO_4$ tetrahedra in hexagonal array with bases roughly coplanar together with hydroxyl ions placed over the centers of the hexagons of the lower layer in which two-thirds of the octahedral sites are occupied by Al ions. The Al ion changes the coordination, from octahedral into tetrahedral, during the dehydration–dehydroxylation process. Due to this, a 380 nm UV emission band is expected in the material, that is characteristic of minerals containing $SiO_4$ tetrahedra with interstitial alkalis that are placed in adjacent positions to Al ions. Similar to several other Al–Si-rich minerals, one would consider that radiation could induce the mobility of the alkalis giving rise to electron–hole centers trapped on apical oxygens (Si–O centre) in the lattice [4]. The recombination of the electrons with the hole trapped adjacent to $Al–M^+$ reduces the presence of ionic charge compensators at the Al sites and induces a 380 nm luminescence emission to $[AlO_4]^o$ centres (aluminium-hole centres, Al–O–Al group) when the given energy is enough [5,6].

Kaolinite, as many other clays (illite or montmorillonite), is a mineral that appears in different geological and archaeological sediments. It is mainly composed of quartz, feldspars and mica. It is therefore of interest to determine if the UV-blue emission of kaolinite can be used for dosimetric purposes to be potentially applied in the field of dating or retrospective dosimetry. In this sense, this paper reports on the characterization of the 400 nm TL emission of kaolinite and the suitability of this material for environmental applications. In particular, the study focuses on: (i) the trap structure and the estimation of the activation energy values of both

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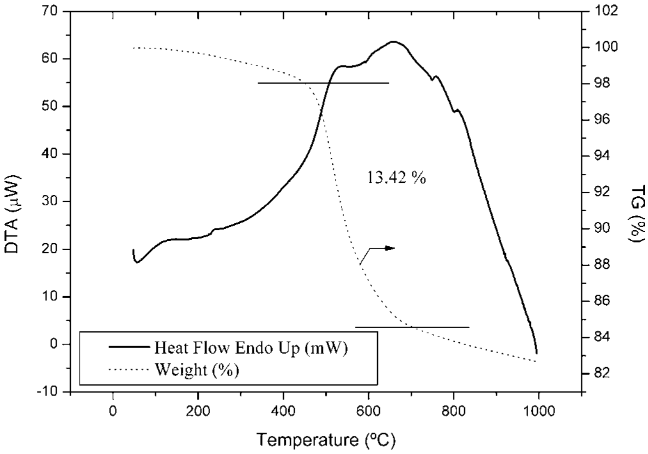

**Fig. 1.** DTA/TG of kaolinite.

natural and induced TL emission of kaolinite; (ii) the stability of the TL signal after six months of storage and (iii) the dose dependence of the 400 nm TL intensity in the range of 50 mGy to 8 Gy. The values of the activation energies have been estimated by initial rise (IR) analysis in both natural and irradiated samples.

## 2. Materials and methods

Natural white and clean kaolinite taken from the final overflow (sized <5 μm) of the industrial hydrocyclone of the Caosil Company (Poveda de la Sierra, Guadalajara, Spain) has been used in this study. The sample was analyzed by of X-ray fluorescence spectrometry, using a Phillips Spectrometer PW 1410/20 with a PW 1730 generator. An Inductively Coupled Atomic Plasma Spectrometer (model ICAP IRIS-DUO of Jarrel Ash Co.) with a CID (charge injection device) detector for complete coverage from 167 nm to 800 nm was also used. The bulk analysis of the kaolinite sample is $SiO_2$ 48.33%, $Al_2O_3$ 34.45%, $K_2O$ 2.32%, CaO 0.66%, $Fe_2O_3t$ 0.72% and Mn 35 ppm, Cu 9 ppm and Ba 35 ppm. The DTA-TG analyses of 50 mg of powdered kaolinite were recorded with a simultaneous DTA-TG thermal analyzer (Setaram, Set Sys 1750) in argon atmosphere. Thermal treatments were performed at a heating rate of 10 °C $min^{-1}$ from room temperature up to 1000 °C, where (i) dehydration process at 100–120 °C, (ii) dehydroxylation in the range of 400–500 °C, and (iii) transformation of kaolinite into metakaolinite at 570 °C has been detected (Fig. 1). The weight loss (13.42%) is mainly due to the process (ii).

Thermoluminescence (TL) measurements were carried out using an automated Risø TL system model TL DA-12 [7], this reader is provided with an EMI 9635 QA photomultiplier and the emission was observed through a blue filter (a FIB002 of the Melles-Griot Company) where the wavelength is peaked at 320–480 nm; FWHM is 80 ± 16 nm and peak transmittance (minimum) is 60%. It is also provided with a $^{90}Sr/^{90}Y$ source with a dose rate of 0.020 Gy $s^{-1}$ calibrated against a $^{60}Co$ photon source in a secondary standards laboratory [8]. All the TL measurements were performed using a linear heating rate of 5 °C $s^{-1}$ from RT up to 550 °C in a $N_2$ atmosphere. Four aliquots of 5.0 ± 0.1 mg each of kaolinite were used for each measurement. The sample was carefully powdered with an agate pestle and mortar to avoid triboluminescence [9]. The incandescent background was subtracted from the TL data.

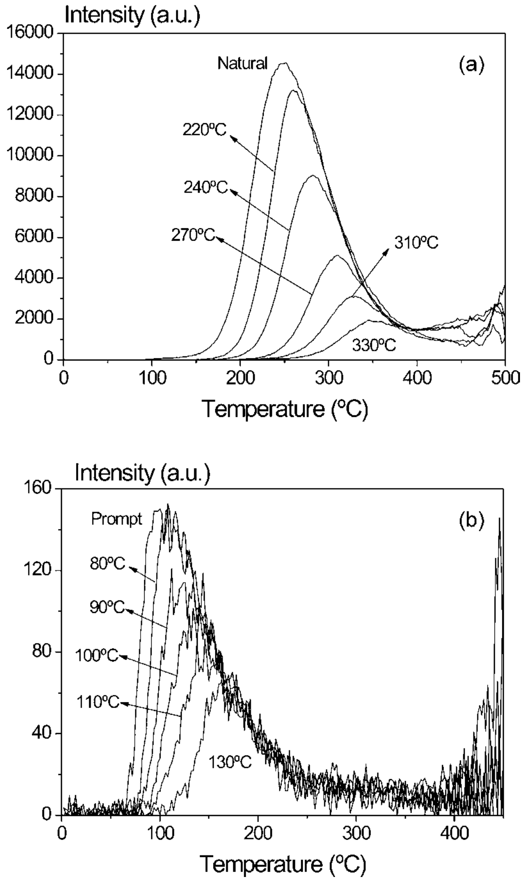

**Fig. 2.** Glow curve of the (a) natural and (b) 1 Gy irradiated kaolinite.

## 3. Results and discussion

The energy trap distribution of the natural and induced TL glow curve of different aliquots of powdered kaolinite (NTL and ITL respectively) has been determined by the following method. Progressive preheating ranging from a $T_{stop}$ of 220 °C up to 310 °C (in steps of 30–40 °C) was performed on the 'as received' samples. It was followed by quenching from the different temperatures to get aliquots with different grades of modulation of the lattice, thus determining the trap structure. Previously to obtain the 1 Gy ITL curves, 'fresh' samples were heated to 500 °C to remove the natural signal. Similar treatments of $T_{stop}$ were given to irradiated samples, but in the range of 80–130 °C (in steps of 20–30 °C) (Fig. 2a and b). The TL glow curves of different aliquots of natural kaolinite (Fig. 2a) are recorded after the preannealing treatment. In the whole natural TL glow curve a broad peak is observed at about 250 °C that should correspond to the starting point of the dehydroxylation process. According to Konan et al. [10] it should involve the transformation of the four $OH^-$ into two water molecules and two $O^{2-}$ that remains in the lattice of the material. The maximum is continuously shifted to higher temperatures as $T_{stop}$ is increased and a change in the shape and intensity of the TL distribution in accordance with the thermal pre-treatment can be observed. The thermolabile broad band of blue emissions shown as TL glow curves indicates continuous processes of electron trapping–detrapping. These thermal phenomena of TL induce consecutive breaking and linking of bonds of Al–O, Fe–O and redox reactions in addition to the aforementioned dehydroxylation process. These processes could be interpreted as being due to a continuum in the trap distribution or to the existence of a tunnelling recombination process [5]. Similar behavior was observed for ITL curves. In both cases, the distribution of traps moves towards higher energies when increasing the annealing temperatures as a consequence of the emptying of the shallower energy traps (see Table 1) but the trap distribution is in a lower energy range in the ITL curves so the

**Table 1**
Calculation of the activation energy values by initial rise (IR) method resulting of the analysis of natural and induced TL glow curves of kaolinite.

| Natural | | | Irradiated | | |
|---|---|---|---|---|---|
| $T_{stop}$ | IR range (°C) | $E$ (eV) | $T_{stop}$ | IR range (°C) | $E$ (eV) |
| 0 | 160–206 | 1.04 (1) | Prompt | 76–86 | 0.85 (6) |
| 220 | 210–230 | 1.15 (2) | 80 | 88–98 | 0.87 (9) |
| 240 | 226–254 | 1.16 (2) | 90 | 88–110 | 0.90 (6) |
| 270 | 250–278 | 1.21 (2) | 100 | 98–112 | 0.94 (4) |
| 290 | 260–296 | 1.22 (1) | 110 | 100–124 | 0.87 (5) |
| 310 | 270–308 | 1.24 (2) | 130 | 110–124 | 0.93 (9) |

maximum of the broad peak consequently appears at lower temperatures.

The activation energy values estimated using the initial rise (IR) analysis of the natural and irradiated glow curves are summarized in Table 1. Previously, the TL curves were analyzed in terms of both first and second order kinetics equations, respectively corresponding to the cases where the intensity of the TL is proportional to the concentration of thermally released charges, and where the thermally released charges are re-trapped at least once before the recombination process. However, the best-fit parameters obtained, based on the value of the figure of merit (FOM), were unsatisfactory; TL emissions of the samples cannot be explained employing the commonly accepted model based on the discrete trap distribution standard since it was not possible to determine some physical parameters such as trap-energies or pre-exponential factors. Therefore, due to the complexity of the TL glow curves, a structure of mixed order kinetics might be tentatively considered. The estimation of the activation energy ($E_a$) using the IR method [11] reveals the existence of traps at different depths. This method is based on the premise that occupancies of the relevant states remain almost constant for the lowest temperature side of the TL peak and, consequently, this side of the peak will follow an exponential dependence regardless of the kinetic order and the applicability of the quasi-equilibrium approximation (1), i.e.:

$$I_{TL} \propto e^{-E_a/kT} \tag{1}$$

where $I_{TL}$ corresponds to the TL intensity, $k$ is the Boltzmann's constant and $T$ is the temperature. Therefore, from an Arrhenius plot ($\mathrm{Ln}\, I_{TL}$ vs. $1/T$) the activation energy can be obtained regardless of any other kinetic parameter. This method for the estimation of $E_a$ values has been satisfactory tested for very complex materials [11]. Fig. 3 displays the Arrhenius plot of the UV-blue emission in the 160–206 °C range for natural kaolinite sample. To the best of our knowledge, the estimation of the activation energy of this material was never reported before. Nevertheless, the activation energies derived from our study have to be considered as a first estimation because they can vary according to the preheating temperature. Therefore, further work is necessary in order to determine a more accurate value.

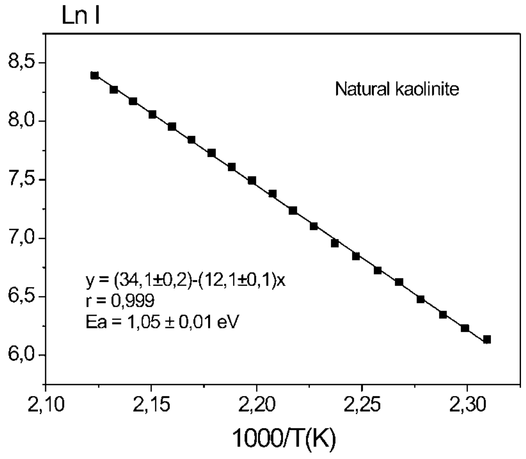

**Fig. 3.** Arrhenius plot of the low-T side of the natural TL UV-blue emission of kaolinite in the range of 433–479 K (experimental data are marked on the fitting line).

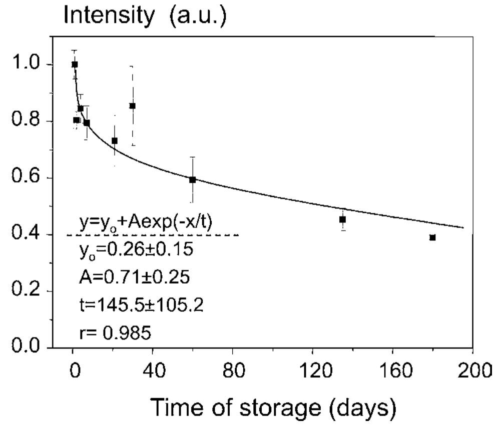

**Fig. 4.** Stability of the blue TL emission over 180 days at room temperature (experimental data and the error bars are displayed on the fitting curve).

The temporal evolution of the TL emission after 1 Gy of beta irradiation is displayed in Fig. 4. For such purpose, samples of kaolinite were preheated up to 500 °C to erase its natural TL. Assuming that the aliquots could exhibit high sensitivity under white light, the samples were stored in red light at RT to prevent trapped electron releasing from semi-stable sites into hole centres, including luminescence centres. Measurements were made after increasing the storage periods of time (up to 183 days) using four replicates each. The calculation of each point was calibrated individually for each aliquot, referring the direct delayed measurement (area of the glow curve in a range of 30–500 °C) to a 1 Gy induced prompt TL glow curve, in the same range of temperature, avoiding the influence of the weight factor. The uncertainties ($1\sigma$) represent the precision of the mean value (MV) of the luminescence response (counts in arbitrary units) corresponding to the group of four aliquots.

As shown in Fig. 4, the fading of the TL emission of this material is close to other materials previously studied under the same conditions [6]. The TL signal starts with an initial rapid decay (ca. 60%) followed by a mild slope that, according to the fitting reaches the stability at a relative intensity of $0.26 \pm 0.15$. The TL signal behavior is associated with the probability of electron release from the shallower traps that occurs very fast at RT. A month later, the electron population decreases asymptotically by the $X$-axis and the involved electrons are located in deeper traps; consequently, more energy is needed to leave their positions at RT. The number of trapped electrons depends on the time that the kaolinite lattice needs to reach up the stabilization after receiving the double treatment of heating and irradiation. This physical process can be fitted to a first order decay equation of the form $y = y_0 + A\exp(-x/t)$ where: $y$ corresponds to the relative intensity of the TL signal, $x$ is the time after irradiation process and $y_0$, $A$ and $t$ are coefficients of the equation. An acceptable value of the regression coefficient of fitting ($r = 0.985$) was obtained. One can assume that the results at room temperature can be well fitted by a single exponential component since only the lowest energy traps of the distribution are involved in the fading process and they can be effectively considered as a single discrete trap at energy $E_0$ [6,12].

The dose dependence of the blue TL emission from this material was also investigated in the range of 50 mGy to 8 Gy. As seen in Fig. 5, the evolution of the whole area of the induced TL peak with the dose shows a very good linear fitting ($r = 0.999$) and can be fit-

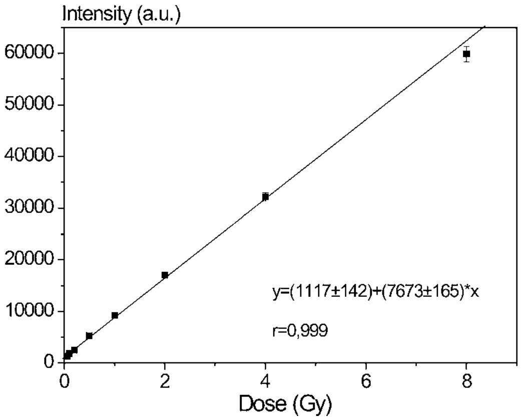

**Fig. 5.** Dose dependence of the TL glow curve in a range of 50 mGy to 8 Gy (measurements and the error bars are marked in the fitting line).

ted to an equation of the sort $y = y_0 + bx$, where $y$ corresponds to the intensity of the TL signal, $x$ is the given dose and $y_0$ is a coefficient of the equation. The uncertainties ($1\sigma$) represent the precision of the MV of the area under the glow curve in a range of 30–500 °C for five aliquots. In the studied range of dose, usually employed in the fields of retrospective dosimetry and dating, no saturation has been detected for any group of components. Despite that radiation may induce displacement of lattice ions or produce electron defects that involve changes in the valence state of impurities atoms and consequently changes in the spectral composition, no modifications could be seen in the blue TL emission of ITL curves with increasing dose.

## 4. Conclusions

The radiation effect on the 400 nm TL emission of kaolinite suggests that this material could be potentially valid for dosimetric purposes since it (i) is sensitive to radiation and (ii) possesses a good dose linearity in the range of 50 mGy to 8 Gy. However, the stability of the TL signal during six months of storage shows an initial rapid decay (ca. 60%) followed by a mild slope reaching the stability after six months. It suggests that the electron population decreases asymptotically and the involved electrons are located in deeper traps at room temperature. The fading process can be fitted to a first order decay equation of the sort $y = y_0 + A\exp(-x/t)$. This unexpected experimental result indicates that only the shallowest portion of the trap distribution is affected at room temperature. Finally, the tests of thermal stability at different temperatures suggest a continuum in the trap distribution.

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