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Thermoluminescence response of the polymineral fraction from *hibiscus sabdariffa L foodstuffs*

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Food processed by ionizing irradiation is a safe technology and has been recognized by the FAO/WHO Codex Alimentarius Commission. It is an excellent method to prevent food spoilage and foodborne diseases by inhibiting the growth of microorganisms and slowing down ripening. The widespread use of food irradiation treatments that include spices, dry vegetables, grains and fruits make relevant the developing of methods for identification and analyses of foodstuffs processed by irradiation. The present work focuses on the thermoluminescence property of Mexican Roselle flower previously irradiated for detection purposes. The polymineral content of irradiated commercial Roselle flower (*Hibiscus sabdariffa* L.) was extracted and analyzed by thermoluminescence (TL). The X -ray diffraction analyses showed that quartz and albite composition of the polymineral fraction. Different grain sizes; 10, 53, 74 and 149 μm, were selected for the TL analyses. The TL glow curves depended on the grain sizes. The glow curves depicted two peaks around 92 and 120°C. The first peak was ascribed to quartz and the broad part of the glow curves (120-250°C) seems to correspond to the albite. Because the complex structure of the TL glow curves from polyminerals the kinetic parameters were calculated by a fitting process using a deconvolution method based on a non-linear least-squares Levenberg-Maquart. The values of the activation energy were found to be at 0.79-1.05 eV and 0.79-1.04 for 53 μm and 250 μm, respectively. The TL properties of the samples were determined including dose response, reproducibly, fading and UV light bleaching.

Keywords: Food irradiation; Roselle flower (*Hibiscus sabdariffa L.*); polyminerals; kinetics parameters.

El proceso por radiación es una alternativa tecnológica reconocida por la FAO/WHO Codex Alimentarius Comisión, conveniente para desinfectar alimentos y lograr la seguridad de los consumidores ante el aumento de enfermedades transmitidas por los mismos alimentos en el mundo. Sin embargo, es necesario desarrollar métodos que logren identificar y analizar propiedades de los alimentos expuestos a radiación ionizante. El presente artículo está enfocado al estudio de las propiedades termoluminescentes (TL) de la flor de Jamaica Mexicana para propósitos de detectar tratamientos con radiación ionizante. Se analizaron por termoluminiscencia la fracción polimineral de la flor de Jamaica comercial (*Hibiscus sabdariffa* L.) de muestras irradiadas. El análisis por difracción de rayos X (DRX) mostró que la fracción polimineral estaba compuesta de cuarzo y albita. Se eligieron diferentes tamaños de grano; 10, 53, 75 y 149 μm para el análisis TL. Las curvas de brillo muestran que la emisión TL depende del tamaño de grano. Las curvas de brillo muestran dos picos principales alrededor de 92 y 120°C. El primero está asociado al cuarzo, y la parte ancha de las curvas de brillo (120-250°C) parece que corresponde a la albita que también está presente en las muestras de Jamaica. El método Tm-Tstop mostró que las curvas de brillo de la flor de Jamaica contiene ocho picos de brillo (100-250°C). Debido a la complejidad de la estructura de las curvas de brillo a diferentes dosis gamma, los parámetros cinéticos se calcularon mediante un proceso de aproximación usando un método de deconvolución basado en mínimos cuadrados no-lineales Levenberg-Maquart. Los valores de la energía de activación referidos a las trampas en la fracción polimineral estuvieron entre 0.79-1.05 eV para 53 μm y 0.79-1.04 para 250 μm, respectivamente. Se encontraron cinéticas de primer y segundo orden. Se evaluaron también las propiedades TL; dosis-respuesta, reproducibilidad de las señales, también el fading y pérdida de TL después de exponerlas a luz UV.

Descriptores: Alimentos irradiados; *Hibiscus sabdariffa L.*; poliminerales; parámetros cinéticos.

PACS: 78.60.Kn; 83.80.Ya; 78.55.Hx

1. Introduction

The food irradiation process is a safe alternative to ethylene oxide or other toxic solvents used frequently for treatment foodstuffs like spices, herbs, flowers, fruits, besides others; in order to disinfect them from contamination by microorganisms. Food irradiation technology has been used in European countries since 1993, after an Expert Committee formed by a FAO/WHO/IEAE joint body recommended [1,2] the use of a 0.03-50 kGy doses range for commercial food processing and a 10 kGy maximum dose for herbs, spices and seasonings-food. Today there are some physical and chemical methods which are widely accepted for detection of previously irradiated food [3-8]. A practical and non-expensive method used for detection of irradiated dried foodstuffs that contain mineral fraction is the thermally stimulated luminescence or thermoluminescence (TL). However, the composition of the inorganic minerals content like quartz and feldspars may change in concentration depending on the different regions and countries [9-17]. In consequence a typical TL response and properties may be found in different mineral samples. The analysis of their thermoluminescence properties allows to evaluate the TL emission properties, kinetics parameters, TL sensitivity and the overall effects of the ionizing radiation doses. The starting point is the polymineral fraction content (quartz or feldspars) of food processed by irradiation which in principle may be irradiated and thermally stimulated to induce the emission of light. After the exposure of the mineral sample to ionizing radiation, charge carriers in the form of electron and holes are created in a number proportional to the irradiation dose, some of which are trapped in trapping centers located inside the band gap, remaining there in a stable manner in spite of room temperature instabilities. Thermal stimulation may release the trapped charges into the valence and conduction bands followed by a radiative and non radiative recombination. The emission of light during thermal stimulation is attributed to a radiative recombination and gives rises to the well-known TL glow curve, usually depicted as curve showing the intensity of emitted light as a function of temperature. The TL glow curve coming from the inorganic polymineral fraction extracted from a previously irradiated foodstuff can be associated to previous irradiation treatments received by the foodstuff [13,17-19] and the main TL features like TL peak components, dose effects, fading, bleaching effects may be evaluated. The aim of this work is to study the main TL characteristics of the polymineral fraction extracted from Roselle flower (*Hibiscus sabdariffa* L.) treated by gamma irradiation, grown as herb and belonging to Malvaceae family, which is widely grown in Mexico and commonly used for food flavoring around the world.

2. Experimental

The Roselle commercial samples were acquired in Mexico. Twenty five grams of Roselle flower was mixed with ethanol-water and kept in constant agitation in order to obtain the polymineral fraction from the samples. To eliminate organic residue fraction, the water was removed and the separated polyminerals were washed with a H_2O_2 solution and distilled water. The polymineral part was washed again in chloride acid and then dried with acetone. The extracted samples were stored in dark condition at room temperature (21-23°C) before and after irradiation. The polymineral identification was characterized by X-ray diffraction (XRD) using a Rigaku Geirgerflex D-Max diffractometer equipped with CuK_α-radiation (λ=1.5406 Å) and graphite monochromator. X-ray patterns were obtained using 40 kV, 20 mA and a scan speed of two degree per minute (2θ). XRD showed that quartz and albite are present in the mineral fraction of the Roselle samples. A micrograph was obtained with a scanning electron microscopy (SEM) JEOL model JSM-5410LV equipped with EDS (Si-Li:Na) detector. The energy-dispersive spectroscopy (EDS) was made for different grain sizes in order to determine the elements present in the mineral fraction samples. The polymineral fraction was separated by different grain sizes; 10, 53, 74, 250 μm. To obtain 10 μm size, the Zimmerman method was used [20]. A 4 mg of powder for each grain size was deposited onto aluminum discs; a drop of acetone was added in order to have a homogenous distribution of the grains. A series of samples for irradiations and readout was prepared and exposed to different gamma doses (1Gy-5 kGy). The samples were exposed to gamma-rays delivered from a ^{60}Co semi-industrial MDS Nordion irradiator, it was calibrated using Fricke dosimetry [21]. The TL measurements were carried out using a Harshaw TLD 3500 reader with 2 K/s heating rate in an inert N_2 atmosphere to reduce spurious TL signals. The effect of the ultraviolet (UV) light and fading by storage at 22°C in darkness were investigated on the samples. Duplicated samples were exposed to the UV using an Hg lamp source, model OS-9286 from Pasco Scientific Company. The lamp had a light beam irradiance of 0.1 μW/cm^2. The TL glow curves structure and the kinetic parameters were calculated based on the Lanberg-Marquard method.

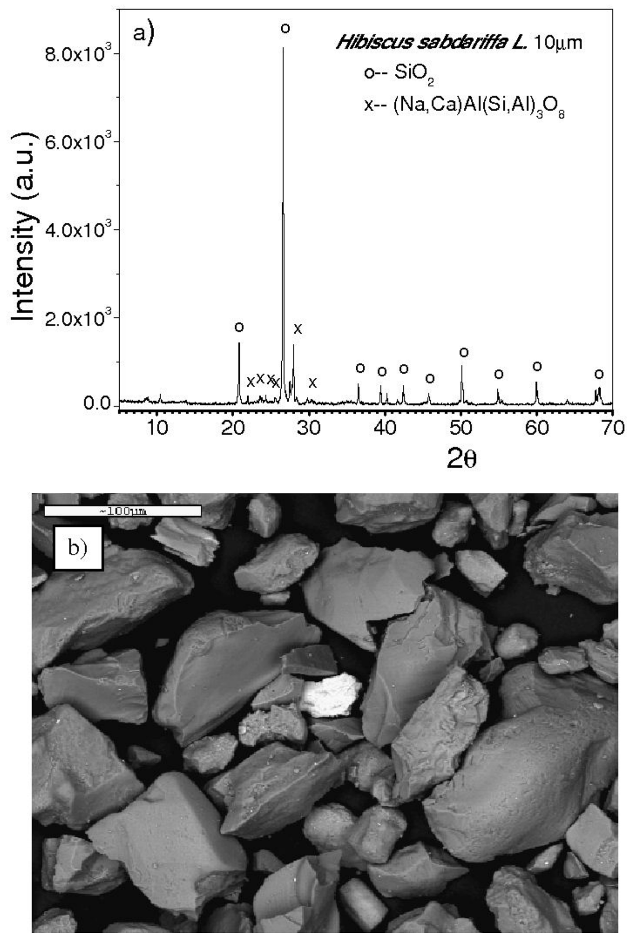

FIGURE 1. a) XRD difractogram of Roselle polyminerals, quartz (SiO_2) and feldspar albite $(Na,Ca)Al(Si,Al)_3O_8$ are present in the samples; b) SEM image of the polymineral sample. On the white region Ti and Fe elements were detected by energy-dispersive spectroscopy (EDS).

TABLE I. Kinetics parameters from glow curves of polyminerals, 53 and 250 μm grain sizes.

53 μm					
Peak	Order	E (eV)	s (1/s)	Area (cnts)	Tm (°C)
1	1	0.95	2.96E+13	1.04E+00	64.5
2	2	1.05	1.19E+14	6.06E+01	84.7
3	2	0.98	8.79E+11	5.26E+01	114
4	2	0.95	4.46E+10	5.37E+01	141.8
5	2	0.92	2.29E+09	4.08E+01	175.6
6	2	0.91	1.01E+07	2.58E+01	287.9
7	2	0.79	9.36E+06	3.49E+01	219
8	1	0.97	4.55E+03	3.99E+03	386.1
250 μm					
Peak	Order	E(eV)	s (1/s)	Area (cnts)	Tm (°C)
1	1	0.95	5.86E+12	4.49E+01	81.1
2	2	1.04	2.60E+13	8.72E+01	99.4
3	2	0.98	4.01E+11	9.09E+01	124.1
4	2	0.94	2.10E+10	9.82E+01	151.8
5	2	0.93	1.48E+09	8.01E+01	186.1
6	2	0.91	1.07E+07	4.76E+01	287.5
7	2	0.79	6.16E+06	7.95E+01	231.2
8	1	0.97	1.59E+04	2.65E+03	312

3. Results and discussion

The X-ray diffraction (XRD) pattern is shown in Fig. 1 a). It displays the main mineral fraction contents in the dust samples of Roselle flower corresponding to quartz, SiO_2, and the feldspar albite, (Na-Ca)Al(Si,Al)$_3$O$_8$, along with the JCPDS card number 46-1045 to identify the inorganic components. Figure 1 b) shows the SEM micrograph of the whole polymineral sample; the grays blocks in the SEM image correspond to quartz, and the white region contained Ti and Fe elements as confirmed by energy-dispersive spectroscopy (EDS). EDS analysis revealed the presence of Tl, Fe, Al, Si, K, Ca, and Ti elements in the polymineral fraction. The EDS measurements were taken on 4 to 6 different regions in the surface on each sample and the same elements were identified in different grain sizes of the polymineral samples with a characteristic element concentration. The elements composition in each sample may influence the TL glow curves structure of the polymineral. It has been documented the effect of feldspar composition on the TL in minerals separated from irradiated foodstuff [22,23]; however, the mechanism of TL in feldspars is still a debatable issue [24-26]. The 10 Gy irradiated TL glow curves for different grain sizes (10, 53, 74, 250 μm), are shown in Fig. 2 a), indicating a broad TL band (36-350°C) with TL peaks maxima around 90 and 125°C . In previous work [27], similar results were found in samples of Roselle flower, from the tropical coast region in México, having quartz, plagioclase and illite in their polymineral composition and a TL glow curves with peaks at 107 and 277°C. In the present case, quartz is the main mineral fraction mixed with albite.

The TL measurements of the maximum peak temperature (Tm) as a function of the end temperature (Tstop) illustrated in Fig. 2 b), reveled a stepwise function indicating the existence of a discrete trap distribution set. However, since there is evidence that quartz and albite are present in the Roselle flower samples, the observed TL is probably a result of the characteristic TL response of each mineral in the form of a broad TL band composed of several overlapped TL components. Because the complex structure of the TL glow curves they were analysed using a method based on the non-linear least-squares Levenberg-Maquart method to fit the experimental data performing a deconvolution of the glow curves and resolving its TL peak components. The obtained values of the FOM (figure of merit) were lower than 1%, indicating a good fit of the experimental glow curves [28]. Figure 3 shows that the structure of glow curves is composed of eight TL peaks having similar kinetics parameter for the 53 and 250 μm grain size samples as indicated in Table I. The activation energy values were between 0.79-1.05 eV and the glow curves followed first and second order kinetics. The performed deconvolution processes indicate that in spite of the complex TL glow curve structure no major differences in the activation energy values with the particle size were found.

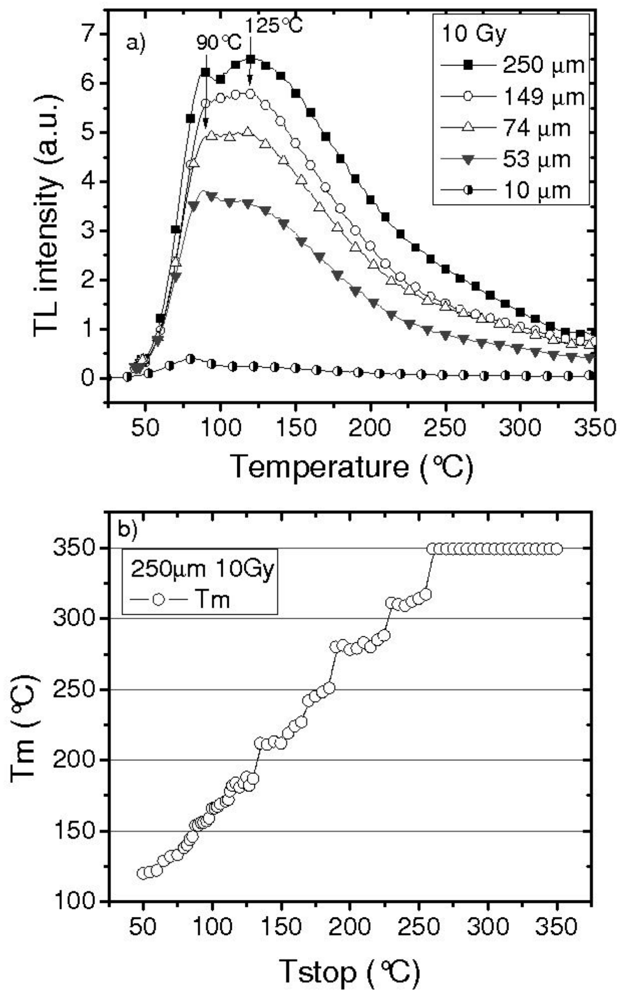

FIGURE 2. a) TL glow curves for different grain sizes irradiated at the same dose 10 Gy; b) The Tm-Tstop behavior shows a stepwise function indicating a discrete trap set.

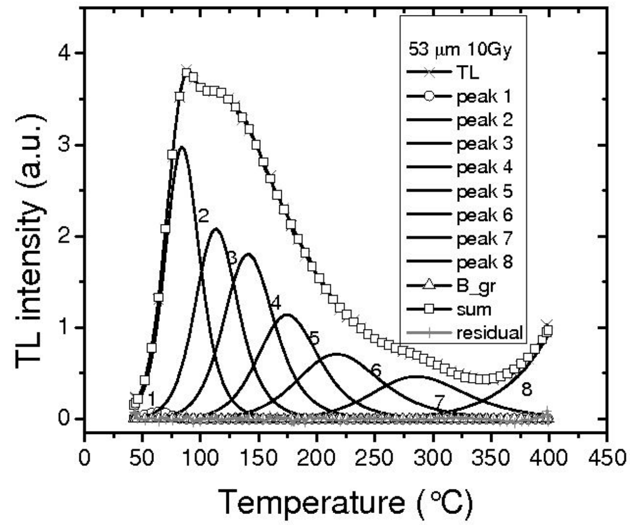

FIGURE 3. Deconvolution of TL glow curves for the polymineral (53 μm) fraction.

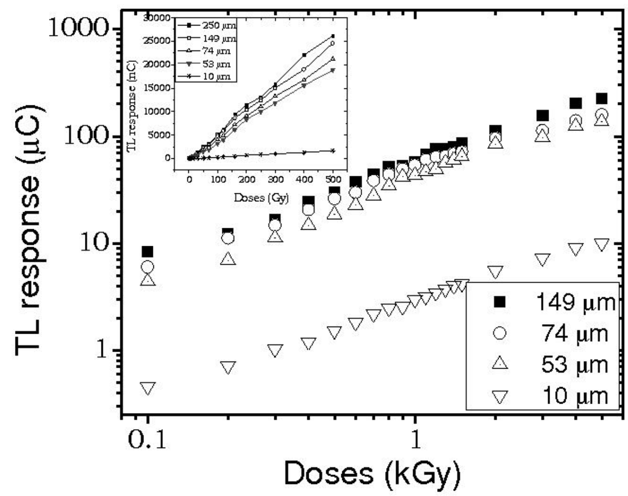

FIGURE 4. TL dose response and its grain size dependence. The inset figure shows the 1.0 -500 Gy dose response.

The deconvoluted glow peak located at 287°C seems very stable under the same irradiation dose (10 Gy) and for different particle sizes, meaning that it would be a good TL peak for dose determination in irradiated foodstuffs.

The TL response as a function of the dose was investigated in the range from 1 Gy to 5 kGy for grain sizes of 10, 53, 74, and 250 μm. Figure 4 shows that the TL response increases as the dose increases begin linear for irradiation doses between 10-500 Gy and for any grain size. Above 1.0 kGy there is a clear saturation of the TL signal. The TL of the 10 μm sample had the lowest TL dose response and increased as the size increases. It has been observed elsewhere [29-31] that the TL glow curve in some polymineral, quartz and feldspars, depends on the different concentration of elements like Al, P, Ti, Ge, Na, Tl, Fe, Si, K, and Ca, which are present in each grain sizes. It is known that the glow peaks about 110 and 325°C in quartz result from the dissociation and recombination of the defect pairs. The 110°C TL peak is the result of a thermally released electron being captured by a hole center. The second peak, 325°C, is from interstitial alkali ions (M^+) being thermally released and recombining at an $[AlO_4]^-$ center. The alkali M^+ ions are mobile and can be captured at a number of defects D_i, to form D_i-M^+ pair and these play an important role in TL sensitization processes [31-33]. In the other hand a strong variation is observed in the TL intensity features of feldspars [34,35] due to feldspar composition. K feldspar exhibits a more intensive TL than Ca rich plagioclase, albite and anorthite [35,36]. In the present case, since quartz and albite are the major present elements in the polymineral content, there is no doubt that the strong TL glow curve intensity is associated to this particular polymineral fraction extracted from Roselle flower (*Hibiscus sabdariffa* L).

The room temperature fading of TL signals was analyzed as a function of the elapsed time after the irradiation process. Figure 5a) shows the fading effect over the period of storage for the 10, 53, 74, 149, and 250 μm grain sizes. The TL fading was measured in darkness over a period of 60 days and

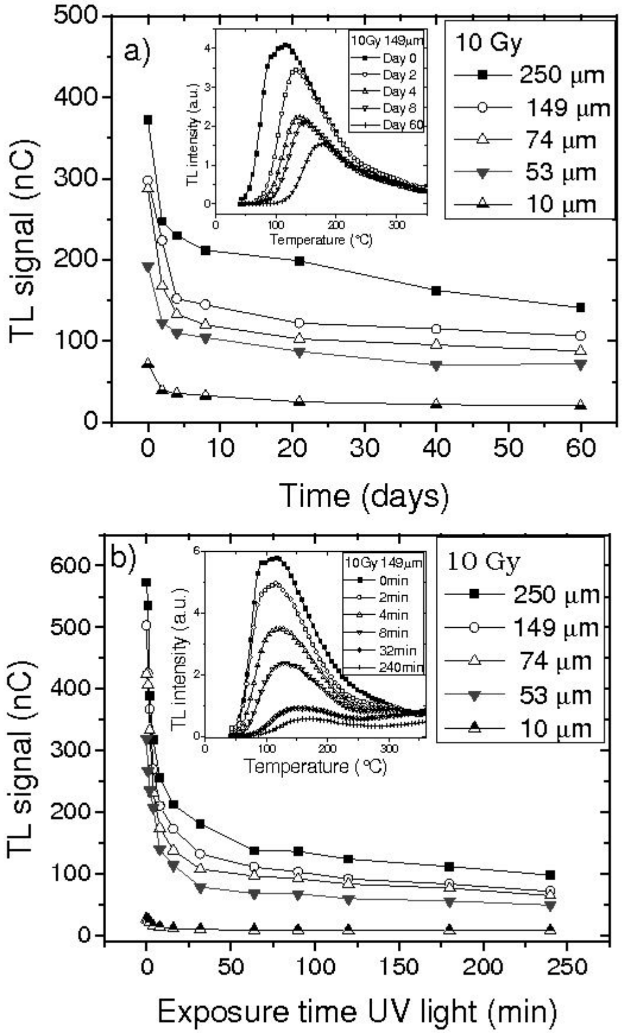

FIGURE 5. a) Fading at room temperature after irradiation of different grain sizes, b) effect of UV bleaching on the TL response. The inset figures show the obtained TL glow curves.

the behavior was very similar irrespective of grain sizes. The TL losses were quite high during the first five days. After that the TL decays decreased to about 30% at the end of the storage time for the 149 μm grain size. The behavior for the other grain sizes was similar. The lower temperature TL peak at 90°C fades out faster than the main TL peak at 125°C and shifts to higher temperature around 175°C at the end of the storage period. This TL fading behavior is very similar to that previously reported in Roselle flower from the tropical coast in Mexico but irradiated at 10 kGy [27] and to that of mint and chamomile in which quartz is the main component of the extracted polymineral fraction [15]. The TL decay characteristics is related to the existence of shallow trapping states and to the discrete trap distribution composed of several overlapped TL glow peak found in polymineral fraction from Roselle flower samples. UV bleaching during 240 minutes of a 10 Gy irradiated polymineral samples were performed and the result is illustrated in Fig. 5 b). The TL UV bleaching losses occurs faster than room temperature fading in darkness with a similar TL decay of the TL glow peaks components indicating a similar detrapping mechanisms, of the discrete trap distribution, behinds the TL fading and the UV bleaching processes. Bleaching experiments in Australian quartz samples exposed to wavelengths less than 400 nm resulted in bleaching of the glow peaks at 160, 220, 325, 370, and 480°C and shift to higher temperature of the main TL peak [37]. These results confirm the present findings related to the presence of a discrete trap distribution and TL fading properties in Roselle flower polymineral samples. In addition, the reproducibility of the TL signal up to 10 readout cycle was found to be better for the 149 μm grain size, having a standard deviation of 3.4%, indicating that the TL response of the polymineral fraction of Roselle flower could be used for TL detection in previously irradiated specimens.

4. Conclusions

The XRD analyses showed that quartz is the main component in the polymineral fraction of Mexican Roselle samples. EDS analysis reveals that Tl, Fe, Al, Si, K, Ca, and Ti elements are present in the polymineral fraction. The glow curves showed two peaks located around 90 and 125°C for different grain sizes of 10, 53, 74, 149, and 250 μm which are ascribed to the presence of quartz. The broad glow curves showed a complex structure composed of eight overlapped TL peaks irrespective of their grain sizes but with higher TL response for larger grain sizes. The TL glow curve analyzed by the Tm-Tstop method revealed the existence of a discrete traps distribution. A deconvolution process involving eight TL glow permitted to determine the activation energy values around 0.79-1.05 eV and the first and second order kinetics for some peaks. The peak located at 287°C seems very stable after exposure to 10 Gy dose and for different particle sizes, indicating to be a suitable TL peak for dose assessment in irradiated Roselle polymineral samples. The TL response was found to be linear in the 10-500 Gy dose range and reproducible in spite of a strong TL fading.

Acknowledgements

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