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Thermoluminescent properties studies of spodumene lilac sample to dosimetric applications

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Abstract. This work investigates the thermoluminescent (TL) dosimetric properties in natural spodumene, $\text{LiAlSi}_2\text{O}_6$, called kunzite, from Minas Gerais State, Brazil. The mineralogical and chemical composition of this material was identified by means X-ray fluorescence and X-ray diffraction. Some dosimetric properties were studied, such as thermoluminescent emission curves as function of gamma dose. The glow curves of annealed kunzite presented two very intense TL peaks at 215 °C (peak II) and 350 °C (peak III), after gamma irradiation, being both of first kinetic order. These two most prominent peaks analyzed do not presented a linear growth in the range of 50 to 5000 Gy in the range of doses studied. The peak II also presented a very short calculated lifetime, which means it is hardly can be used in dosimetry, while the peak III has a longer lifetime and could be used in some applications for high doses dosimetry.

1. Introduction

Spodumene ($\text{LiAlSi}_2\text{O}_6$) is a natural lithium aluminosilicates mineral of significant technological interest. Depending on temperature and pressure, it has been observed in either C2/c (α -spodumene) or P2₁/c (β -spodumene) symmetry [1]. There are three varieties (thiphane, kunzite and hiddenite) of beautiful coloration that are considered as semi-precious gemstones. Besides, the natural crystal is strongly luminescent under UV, electron beam or X-ray excitation. These optical characteristics are caused by lattice defects which exist in natural samples. The most frequent are exchange of Si^{4+} and Al^{3+} ions and the presence of different impurities on substitution and interstitial sites [2-5].

On exciting the samples by ionizing radiation, electrons and holes can be trapped by these sites. They can be thermally released from traps causing a radioactive recombination and thermoluminescent peaks. The characterization of the thermoluminescence properties in aluminosilicates is of special interest for solid state dosimetry applied to dose reconstruction and dating [6-7]. Its striking luminescence turns the spodumene an interesting material to be applied as dosimeter and/or scintillator. However, there is no much information about this potentiality in literature.

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The use of thermoluminescence (TL) in radiation dosimetry requires knowledge of the TL properties of the material. Besides the necessary care during the experiments, it is vitally important the knowledge of the curve shape of the emission and the answer depending on dose, which can be presented as a theoretical model able to predict results. They also provide explanations of the material in terms of its internal structure and the lifetime of the peak. This lifetime is indirectly calculated using the kinetics activation energy (E), the frequency factor (s) and kinetic order (b) [8].

In this work we report some thermoluminescent properties of a natural kunzite (or lilac α -spodumene) from Minas Gerais State, Brazil. In order to derive reliable values of the dosimetric properties two different methods (peak shape and curve-fitting) of TL glow peaks analysis were studied, as well some calibration curves showing the dose range for spodumene TL response.

2. Experimental Details

The natural lilac spodumene sample was obtained from Minas Gerais State, Brazil. The mineralogical composition of this material was identified by means of X-ray diffraction and its impurity content was analyzed with X-ray Fluorescence (XRF). According to previous paper, the lilac color of kunzite is correlated with the presence of Mn and with a low Fe/Mn ratio [9]. The lilac color occurs whenever the concentration ratio of Mn/Fe is larger than 1. The sample here investigated presented the Fe/Mn ratio of 1.11, showing a lilac color in the c -axis direction and a pale yellow in the other directions.

The crystal was ground into powders and sieved to retain the grains between 0.080 to 0.180 mm. Gamma irradiation was carried out at room temperature (RT) using a ^{60}Co source with a dose rate of 7.5 kGy.h^{-1} . For pre-irradiation heating process, the samples were annealed in normal air atmosphere at 600°C for one hour and cooled to RT suddenly.

The glow curves were obtained from a Daybreak 1100 series automated TL reader system equipped with a photomultiplier EMI 9635B and they were recorded from RT up to 500°C , with a heating rate of 4°C.s^{-1} in a nitrogen atmosphere. The TL spectra were recorded using a homemade TL reader equipped with an Unicom 100-FUNBEC monochromator with an accuracy of 5.0 nm, the light being detected by a Hamamatsu 551S photomultiplier.

3. Methods

In the TL models, the probability per unit time for any electron leaving the trap is given by

$$p = s \exp(-E/kT)$$

where s is the frequency factor, E the activation energy, k the Boltzmann constant and T the temperature in which occur thermal liberation.

The lifetime of TL peaks is nothing but the inverse of p :

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

As theoretical methods to calculate the kinetic parameters, E and s , it was employed the Peak Shape and the Curve Fitting Methods. Both are based on the glow curve shape [8,10].

Curve fitting (CF)

The Curve Fitting Method assumes, for a first order kinetics, that the intensity of the glow peak is given by

$$I(T) = n_0 s \exp(-E/kT) \exp\left[-(s/\beta) \int_{T_0}^T \exp(-E/kT) dT\right]$$

This method consists in to solve numerically the previous integral. The computed curve is then compared with the actual experimental curve and a root-mean-square (RMS) deviation between the both is calculated. The procedure continues by sequentially changing the E and s values until a minimum value of the RMS deviation is obtained.

Peak shape (PS)

The method based on the TL Peak Shape utilizes just two or three points from the glow curve. Usually, these are the temperature at the peak maximum T_m and either the low- and high-temperature half-heights at T_l and T_2 . The activation energy can be calculated through the Chen's formula

$$E = c_y (kT_m^2 / \gamma) - b_y (2kT_m)$$

where γ is $\omega = T_2 - T_l$, $\tau = T_m - T_l$ or $\delta = T_2 - T_m$.

The constants c_γ and b_γ for the 1st kinetic order are given in table 1.

Table 1. The constants c_γ and b_γ for the 1st kinetic order

	ω	τ	δ
c_γ	2,52	1,51	0,976
b_γ	1,0	1,58	0

4. Results and discussion

The figure 1 shows X-ray diffractogram of the samples not annealed and annealed at 600 °C during 1 h. In both cases the crystalline structures correspond to the pattern of the natural α -spodumene that has the main planes appointed in the figure.

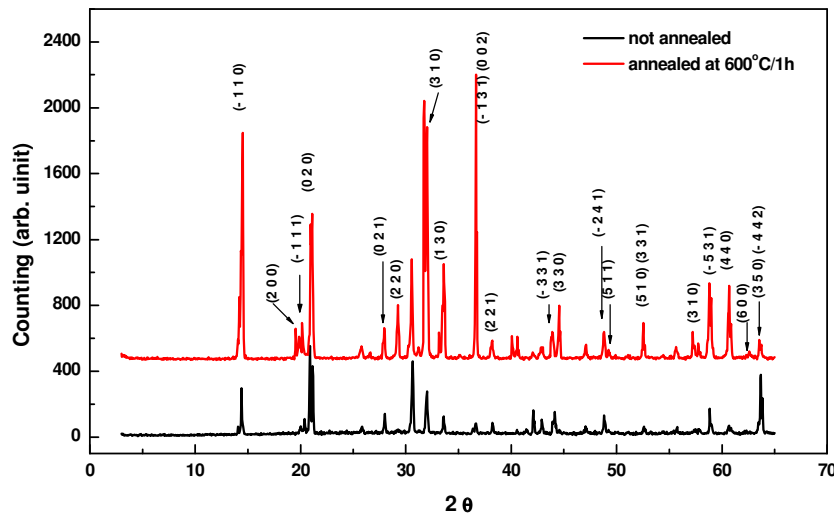


Figure 1. X-ray diffractogram of the not annealed and annealed at 600 °C during 1 h samples. The numbers between brackets are the reflection planes from the α -spodumene pattern.

Some glow curves of the not annealed sample irradiated with different gamma doses are shown in figure 2. There are two most prominent TL peaks around 230 and 430 °C, called peaks II and IV, respectively. This was previously reported by Souza et al. [11]. The peak at 230 °C is more highlighted with respect to the dose increment, unlike of the peak at 430 °C which looks like to disappear with higher doses. The peaks do not change their temperature position as dose increases that lead one to conclude they are of first kinetic order.

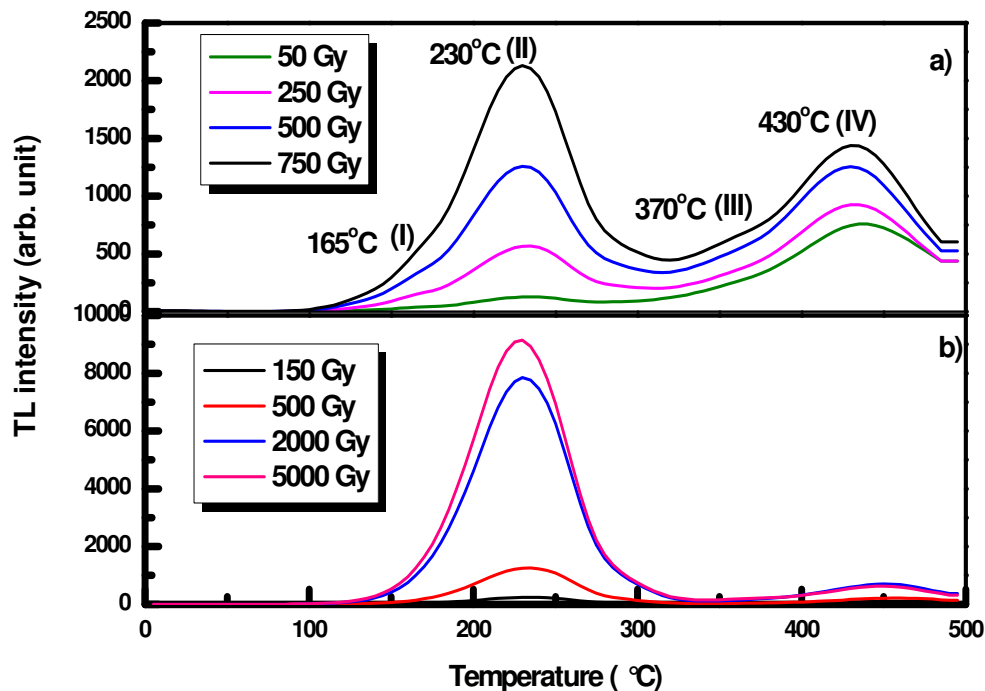


Figure 2. Glow curves of the not annealed sample irradiated in different gamma doses range, from 50 to 750 Gy (a) and from 150 to 5000 Gy (b).

As the main objective was to characterize the spodumene for applications in dosimetry, the focus of this work was given for samples annealed at 600 °C for 1 h and subjected to varied gamma radiation doses. In Figure 3, in contrast to the not annealed, the annealed sample do not present the higher temperature peaks up to 50 Gy, but only one emission around 215 °C, which turns very prominent with increasing radiation dose. However, it is approaching to saturation at about 500 Gy. Unlike, the higher temperature peaks from 500 Gy become easily seen, being the most intense one around 350 °C. However, it is clear that there is more than one peak for temperatures above 300 °C. There must be at least 3 of them at 350, 370 and 460 °C. Moreover, one can perceive the presence of a "shoulder" on the peak of 215 °C, around 145 °C. As the latter must have a very low stability at RT, it decays rapidly after the irradiation and before the TL reading, and thus it is very difficult to follow its actual behavior. It must be done in lower temperatures. Here again one can conclude that most prominent peaks are of first kinetic order, because they do not change their temperature position as dose increases.

Comparing figure 2 and 3, it is noticeable that the more prominent peak in both glow curves have different characteristics. Besides having been moved to a slightly lower temperature (from 230 to 215 °C), it is more intense in the annealed sample. It is also quite clear that the annealing favored the appearance of peaks at higher temperature with higher doses, suggesting that heating causes an increase in the number of deep traps, reducing the number of shallower traps. Another important observation is that there is no change in the position of the peak with the radiation dose increment, which is an indication that it is of first kinetics order and favors its use in dosimetry. This change in the shape of the curve, especially with the appearance of the peaks at higher

temperatures, can be used to the identification of the thermal history of the sample, which is important in geology, for example. After all, if the crystal suffered a annealing at 600 °C it will show only the 215 - 230 °C peak with to doses up to 150 Gy, while the not annealed sample will display principally the higher peaks at 370 and 430 °C.

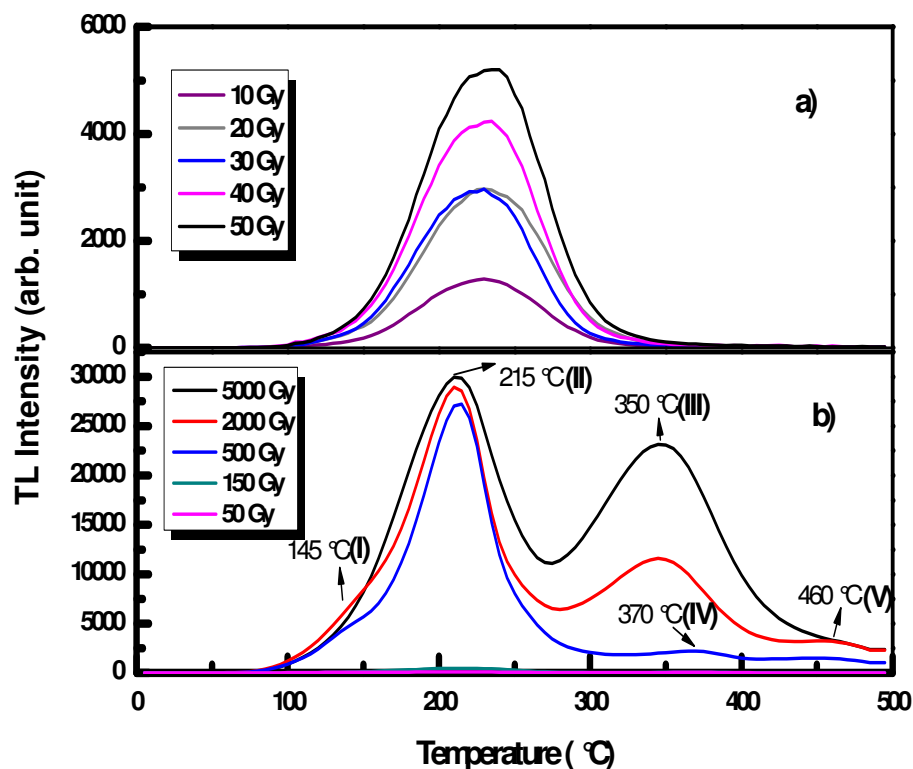


Figure 3. TL glow curves of the annealed samples at 600 °C during 1 h with additional gamma irradiated dose: (a) low dose and (b) high doses. Heating rate is 4 °C/s.

To assess more precisely the behavior of the TL intensity of each peak observed it was plotted their TL intensity versus gamma dose. For not annealed sample, figure 4, it appears that the all the TL peaks have a similar behavior, with an initially sublinear growth, followed by supralinearly region up to about 1500 Gy, entering in saturation around 2 kGy. For annealed sample, figure 5, their behavior is slightly different. Initially the present a sublinear growth, followed by supralinearly region up to about 500 Gy, entering in saturation at about 1 kGy.

An explanation of the supralinearity of the TL response is given based on a model with two traps and a recombination center. Empty traps are filled, initially, linearly with radiation dose. One of the filled traps results in the TL peak in the studied temperature region while the other may be a thermally disconnected deep trap, i.e., a TL peak resulting in an upper temperature region. Both traps compete to capture electrons from the conduction band during irradiation. In this context, the supralinearity occurs when the deep trap saturates before the trap shallower, thus leaving to compete for the capture of electrons. In this case, the shallower trap is then filled with a higher rate. If the resulting rate during the transition between the two regimes is more than linear, it is then

called supralinear. In spodumene, there is the possibility that traps corresponding to peaks at higher temperature than the here studied are responsible for supralinear behavior of the TL peaks between RT and 500 °C. This behavior does not preclude the use of these peaks in thermoluminescent dosimetry, only complicates their use due to the fact that the growth curve must be well established for evaluating the dose received by a spodumene dosimeter in future.

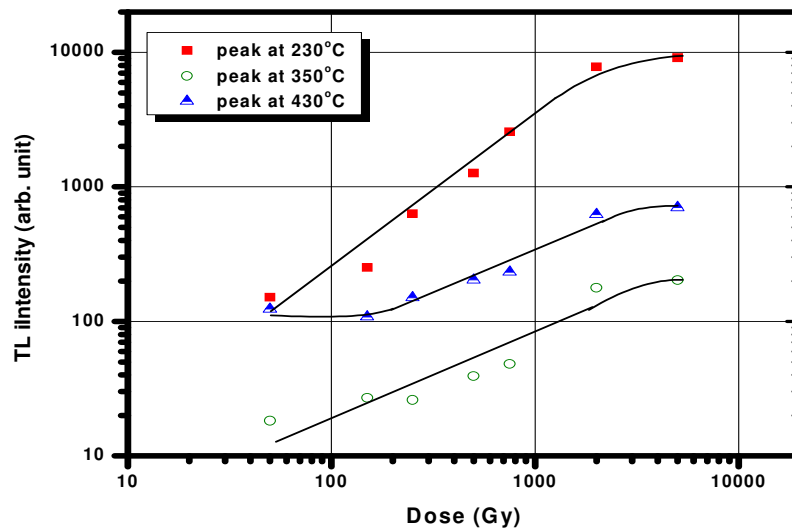


Figure 4. Behavior of the three main TL peaks as function of the gamma dose increment from the non annealed sample

It was calculated the frequency factor, activation energy and the lifetime to the most prominent glow peaks of pre-annealed sample using curve fitting and peak shape methods, being the results shown on the table 2. The different methods applied produced small differences in the parameters. As can be noted, the lifetime of these TL glow peak is slight sensitive to the calculated method, however they are in the same order of magnitude, being the peak 215 °C of about 60 days and the peak 350 °C of about a hundred days.

Table 2. Kinetic parameters resulting from the analyses of the TL main peaks of lilac spodumene. The peaks were considered of 1st order kinetics. (Methods: PS - Peak Shape and CF - Curve Fitting)

Peak temperature	Activation energy (eV)	Frequency factor (s^{-1})	Method of analysis	Lifetime at 15 °C
215 ± 1	0,87 ± 0,04	1,6 ± 0,4)	PS	67,0 ± 0,6 d
215 ± 1	0,82 ± 0,01	(0,4 ± 0,5)	CF	58,0 ± 0,4 d
350 ± 1	0,91 ± 0,10	(0,08 ± 0,60)	PS	106,0 ± 1,2 y
350 ± 1	0,971 ± 0,005	(0,24 ± 0,30)	CF	330,0 ± 0,8 y

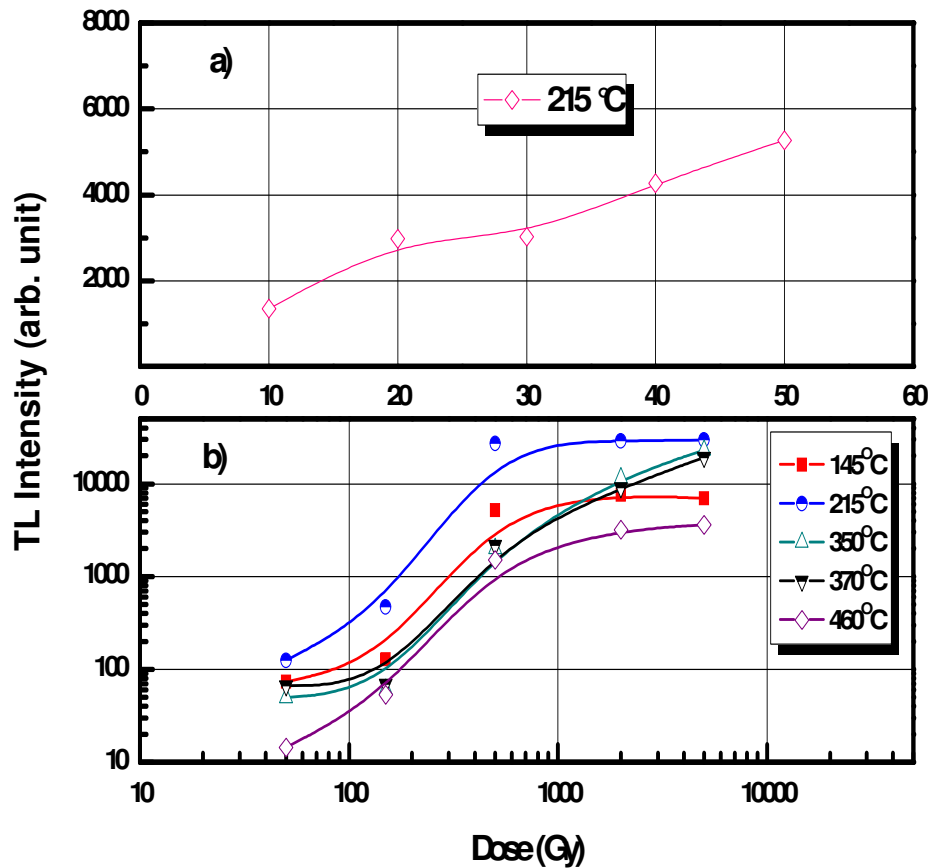


Figure 5. Behavior of the TL peaks of the annealed sample at 600 °C during 1 h as function of the increasing of the gamma dose. a) only the principal TL peak (215 °C) with doses between 10 and 50 Gy b) all identified peaks with doses of 50 to 5000 Gy.

Although the simulation has resulted in a slightly better fit for general order kinetics to 215 °C peak, the difference in settings was not very significant and the order of kinetics was found $b = 1.22 \pm 0.05$, which is also very close first-order. Therefore, the results seem to indicate that the peak is that of the first order, confirming the preliminary assessment. This approach was also found to the 350 °C peak, confirming a good approximation to the possibility of first-order kinetics.

5. Conclusion

The present work was focused on studies of the dosimetric properties of the lilac α -spodumene. The behavior of the TL intensity of the peaks was analyzed as a function of increasing dose, and the main peaks did not show linear behavior, which is desired in a good dosimeter. However, the steps in doses increments were high, and there is the possibility to have a linear behavior in lower dose ranges, mostly between 100 and 1000 Gy, which should be investigated.

The lifetime was calculated using the temperature of 15 °C, as is usually done in literature. The values found were about 2 months to peak at 215 °C, which is relatively short, but indicates that the spodumene may be used for retrospective dosimetry in cases of radioactive accident if the

elapsed time of analysis is less than 2 months. The lifetime of the peak at 350 °C is about a few hundred years, which is short for geological dating, but could be used for dosimetry. However, this peak is not well defined as at 215 °C which makes it difficult to use. It is necessary to apply more methods and techniques to confirm their possible applications.

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