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Thermostimulated luminescence sensitivity changes in biotite-granitic quartz as a result of annealing

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Abstract : The TSL sensitivity change can be observed usually after the quartz is heated to a high thermal treatment In literature, the change of 110°C TSL peak was reported to be an increase in many studies In the present investigation, the change in 150°C TSL peak sensitivity as a function of annealing temperature and annealing time was demonstrated Granitic quartz shows there is slow enhancement in sensitivity up to 800°C. Below 200°C, negligible effect of sensitivity was observed. The number of peaks present in the glow curve and its order of kinetics is found by partial heating method and are confirmed by dose response. The trap population is a trap geochronometer to date a cooling age of a granitic host, if the TSL sensitivity is a measure of the population of associated TSL traps.

Keywords : Thermostimulated luminescence, granitic quartz, annealing effect

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1. Introduction

Thermostimulated luminescence (TSL) is a widespread phenomenon and is exhibited by a host of minerals, organic crystals, glasses and ceramics, organic compounds such as polymers including polyethylene and teflon, certain biochemicals and biological materials. The materials used in radiation dosimetric applications have only been most widely studied for their TSL behaviour. Most of the TSL phosphors can be prepared easily in laboratory. Some of the natural minerals have also been studied extensively for their TSL characteristics because of their applications in archaeology and geology. Especially, feldspar and quartz are two most commonly analyzed minerals in luminescence dating of geological materials and are playing an increasingly important role in retrospective dosimetry

In the present study, an attempt has been made on the TSL glow curve characterisation of quartz separated from white granites of Western Ghat bits near Rajapalayam, Tamil Nadu. According to Han *et al* [2], sediment quartz is a mixture from different origins, such as volcanic and metamorphic quartz. The TSL sensitivity of quartz from each origin may be changed in a unique way for the same annealing. Sediment quartz grains suffered weathering which might have effects on their TSL sensitivity. Unlike the quartz in pottery, granitic quartz was not artificially heated. Due to this reason, granitic quartz was chosen for this study.

The effect of various pre-treatments upon the TSL from Quartz have been reported in literature [3-6]. The enhancement of TSL sensitivity of 110°C peak of quartz was described or addressed to be the result of an increase in the number of activated luminescence centers [3]. More practitioners found a large sensitivity enhancement of the 110°C TSL peak after high temperature annealing [7-9]. The enhanced sensitivity after high temperature annealing was suggested to be not a pre-dose effect [8]. This suggestion was confirmed by a clear enhancement of PTTL sensitivity in a sediment quartz sample after high temperature annealing [10].

The present paper reports TSL characterization of quartz separated from white granites. The change in 150°C TSL peak sensitivity as a function of annealing temperature is evidenced. The different annealing treatments have been demonstrated for the samples. The number of peaks present in the glow curve

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and its order of kinetics are found by partial heating method and are confirmed by dose response.

2. Materials and methods

The white granitic samples collected from twelve different sites (NMP-1 to NMP-12) of Western Ghat bits, Rajapalayam, Tamil Nadu, were used in the present study. Quartz grains were obtained after applying the heavy liquid separation and HF etching and used for TSL measurements. The structural vibrational parameters of quartz were verified through Fourier transform infrared spectroscopical analysis (FTIR).

All these crystals were crushed and ground carefully with a mortar and pestle, washed for 2min with 1% HCl solution and finally with distilled water to remove the organic material if any and then dried. Grains available between 125 - 250μ in diameter, subjected to the above treatment, are used for the TSL measurements. Certain elemental impurities, especially heavy metals such as Fe, Cu, Co and Cr in any material may drastically reduce the intensity of the luminescence emission [11]. The magnetic particles such as Fe, were removed using a suitable powerful magnet to minimize the absorption of TSL signals. Extra care was taken to keep all the samples in the dark until the TSL measurements were taken.

Thermoluminescence measurements were carried out using Nucleonix TLD-96 reader. Powdered samples were heated linearly at a rate of 10°C/Sec. up to 500°C to obtain the glow curve. The heating strip used here is Kanthal strip, which is of composition (72% Fe, 23% Cr, 3% Al and 2% Co). The amount of the sample used for each measurement was 10 mg and an average of four measurements were made for each sample, for accuracy. An optical filter was inserted (in between heating strip and detector) to minimize the response to blackbody radiation. The data was fed to a computer and the black body radiations were digitally subtracted. The gamma source ^{60}Co was used for irradiation.

3. Results and discussion

3.1. Glow curve characteristics :

A representative glow curve of granitic quartz with different treatments is shown in Figure 1. It explains the glow curve characteristic of natural, natural plus irradiation induced TSL (test dose 50Gy) and natural plus irradiation of annealed sample. The natural thermoluminescence (NTL) glow curve of the sample consists of two glow peaks appearing at 150°C and 215°C ('a' in Figure 1). The sample was irradiated by ^{60}Co-gamma source, dose level of 50Gy, and the glow curve shows two new higher temperature peaks at 305°C and 385°C. At the same time, the NTL peak at 215°C is found to be sharp with increase in the intensity, but there is no change in the peak position of 150°C except for the enhancement in intensity ('b' in Figure 1). The samples on irradiating after annealing at 500°C for 1hr with a dose of 50 Gy shows the same four glow peaks with further increase in intensity ('c' in Figure 1). It is observed that the low temperature glow peak (150°C) is predominant over the higher temperature peaks. Generally, in quartz (other than granitic quartz), the TSL of low temperature peak at 110°C is intense relative to all the other peaks. According to Han *et al* [2] the granitic quartz consist of only two glow peaks appearing in the range of 130 to 150°C and 300 to 400°C. But, present study demonstrated four glow peaks.

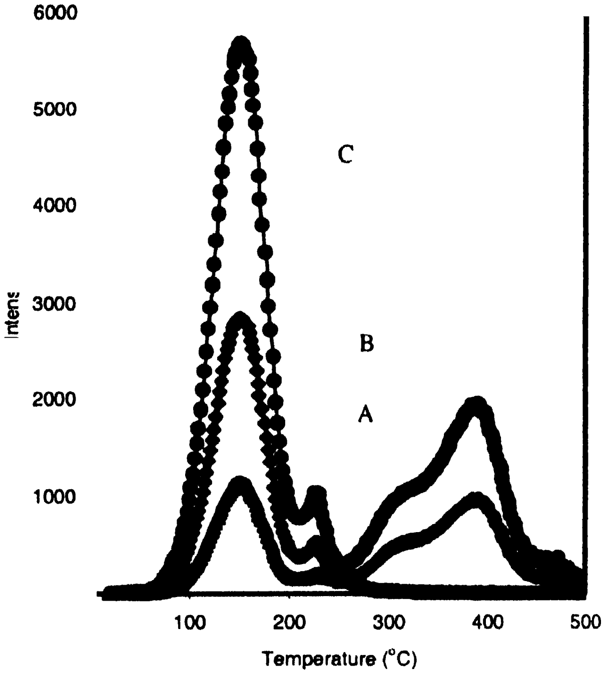

Figure 1. TL glow curve characteristics of quartz (A) NTL (B) NTL+Dose (C) annealing at 500°C for 1 hr + Dose.

3.2. Effect of annealing temperature :

The samples annealed from 50°C to 1000°C with an interval of 50°C for 1hr duration in air atmosphere were irradiated with a test dose of 50Gy and sensitivities of each glow peak are shown in Figure 2. From this, it is observed that the sensitivity does not vary with annealing temperature up to 400°C, thereafter; it has enhanced continuously up to 900°C. A very sharp enhancement is observed in the region of 800 to 900°C. On further annealing above 900°C, the sensitivity is reduced for all glow peaks. The samples annealed at 900°C for 1hr, cause an increase in intensity of the TSL peak of 150°C by a factor of 5, whereas in case of 215°C, 305°C and 385°C peaks sensitivity variations are very less.

From the above observations, the TSL sensitivity of 150°C is independent of annealing temperature upto 400°C. A slight enhancement upto 500°C, a gradual enhancement upto 800°C and a rapid increase upto 900°C are observed, after that it is reduced. According to Han *et al* [2] the 130-150°C TSL peak was independent of the annealing temperature upto 200°C, a rapid increase appeared with the temperature for annealing at higher temperatures. They found an increase of about 10^4 times for annealing at ~1000°C. But the present study shows an increase of about 10^5 times for annealing at 900°C itself. They also observed that the TSL sensitivity of 350-400°C peak changes with annealing temperature in four stages (i) less than 200°C had negligible effect on TSL sensitivity, (ii) annealing temperature from 200 to 300°C gave a dramatic decrease in sensitivity change by about 50%, (iii) annealing temperature from 300-700°C, changed sensitivity a little bit with temperature and (iv) annealing temperature >700°C enhanced the TSL sensitivity very sharply [2]. But in the present investigation, there is no such drastic decrease in sensitivity for annealing temperature from 200 to 300°C. The other observations are almost similar to that of Han *et al* [2].

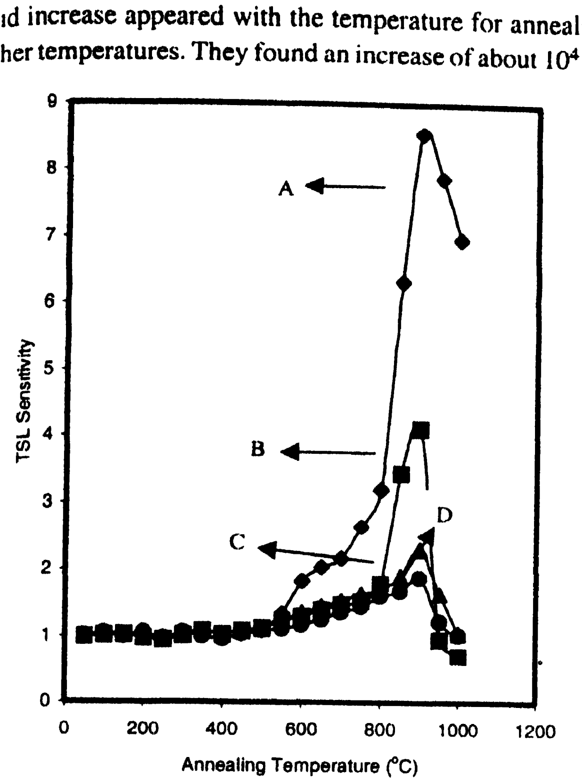

Figure 2. The TL sensitivity as a function of annealing temperatures (50 - 1000°C) for each glow peak (A) 150°C, (B) 215°C, (C) 305°C and (D) 380°C

3.3. *Effect of annealing time :*

To investigate the effect of annealing time on the TSL sensitivity, the samples were annealed at 200°C, 300°C, 400°C, 500°C and 900°C, for different time periods with the identical gamma dose of 50Gy. The sample annealed at 200°C for 15 hr shows that there is no change in its sensitivity (see A in Figure 3). In case of annealing at 300°C for 15hr, the 150 and 215°C TSL peaks sensitivities are enhanced systematically with time and also other peaks are enhanced with less sensitivity (see B in Figure 3). For annealing at 400°C, the sensitivities of 150 and 215°C TSL peaks are increased systematically and for the higher temperature peaks at 305 and 385°C TSL, sensitivities reduced upto 12 hr and then increased (see C in Figure 3). At the same time, the sensitivities of all the TSL peaks are increased with annealing time when the sample is annealed at 500°C (see D in Figure 3). A negligible change is observed for all the peaks when the annealing temperature is ≤200°C. Similarly, the variation in TSL sensitivity as a function of annealing time is shown as E in Figure 3 for 900°C annealed sample. The observed results indicate that TSL enhancement is time dependent. The TSL sensitivity increases upto 10hrs, after that, it reaches saturation for all glow peaks. The same procedure is repeated by cooling in furnace and in air and their results are tabulated in Table 1. From this table, it is clearly shown that the TSL sensitivity is higher when quenched in air as compared with that cooled in furnace. This result was attributed to the impurities distribution throughout the sample which is affected by the cooling rate. The rapid cooling may freeze the impurities and vacancies that

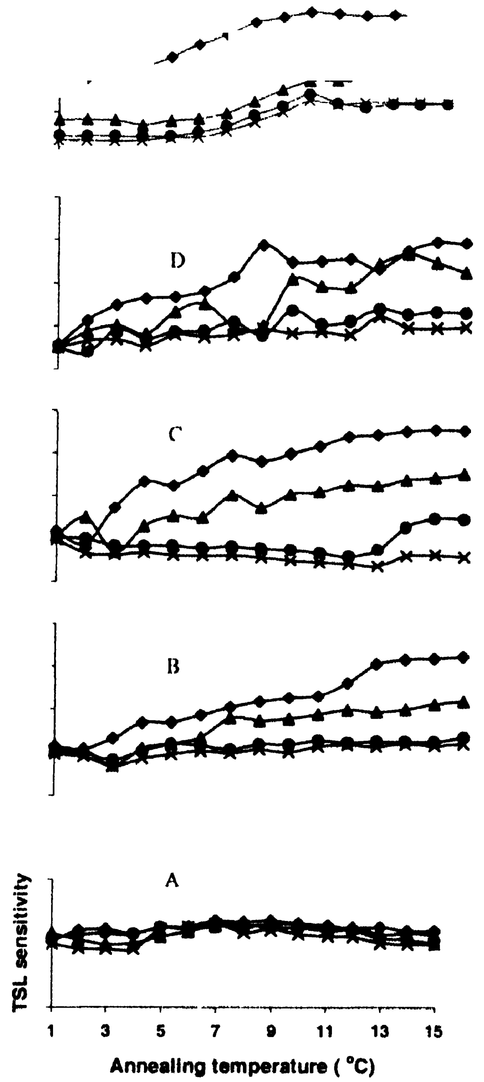

Figure 3. The TL sensitivity changes as a function of annealing time periods at (A) 200°C, (B)300°C, (C) 400°C, (D) 500°C and (E) 900°C for the glow peaks 150°C (◆), 215°C (•), 305°C (●) and 385°C (x)

exist at the higher temperatures, whereas slow cooling allows the formation of aggregates of the impurities [12]. With the view of Han *et al* [2], the peak in the range 130-180°C shows a maximum sensitivity after annealing at 900°C for 1h. But they do not show the optimum condition to get the maximum sensitivity by varying the time period at maximum annealing temperature 900°C. Therefore, the present results evidenced that the annealing treatment at 900°C for 10hr is found to be the optimum condition for TSL sensitization of granitic quartz by rapid cooling. This type of investigation has so far not been observed in quartz.

Table1. A comparative study of TSL (150°C) sensitivity of samples annealed at 900°C for 5hr at different cooling rate (values are shown as the mean value of 15 measurements)

Granitic quartz number	TSL sensitivity Quenched in air	TSL sensitivity Cooled in furnace
1	16.33±0.15	10.55±0.21
2	16.02±0.18	10.19±0.23
3	16.72±0.14	9.99±0.21
4	17.05±0.17	10.77±0.27
5	16.32±0.13	10.38±0.24
6	18.56±0.12	10.87±0.23
7	16.29±0.18	10.65±0.28
8	16.20±0.13	10.41±0.26
9	16.66±0.15	10.34±0.29
10	16.09±0.14	10.72±0.22

In literature [3-11], the TSL study shows that 110°C glow peak is the main characteristic peak of quartz in the form of natural as well as synthetic. But the present study shows a peak at 150°C and it is believed to be similar to that peak observed elsewhere. The annealing always induces an enhancement if the temperature is higher than 200°C. According to Han *et al* [2], high temperature (350-400°C) TSL sensitivities of granitic quartz, annealing at a temperature of about 200 upto 800°C can cause to decrease. A decrease to the level of about 20% of its natural value was observed for the most effective annealing. But the present study shows that all the four peaks are gently increased after 400°C annealing. There is no observation of reduction in sensitivity with annealing time. At the same time, the behaviour of annealing time shows that the sensitivity is gently increased above 200°C for all the four peaks except for 400°C annealing. Annealing at 400°C for different time periods demonstrated that the TSL sensitivity of 150°C and 215°C peaks are increased systematically but 305°C and 385°C peak sensitivities are decreased up to 12 hrs.

In quartz, the luminescence pathways are quite complex. Since it is impossible to distinguish between the luminescence centre and TSL traps in this study, the TSL sensitivity is regarded as a measure of the population of associated TSL traps only [13]. So the TSL sensitivity of the present results can be explained on the basis of trap population. It is assumed that annealing can create new thermally sensitive traps resulting in an increase of their population. The radiation sensitive traps are stable when the temperature is lower than 200°C. After 1hr annealing at 400°C, a decrease in sensitivity indicates that the radiation sensitive traps are destroyed. The cooling age of the granitic sample is obtained after the estimation of initial number and decay rate [2]. Thus, the age estimated should also be the cooling age since the granitic quartz is last cooled to 200°C.

3.4. Dose response :

The granitic samples were exposed to different gamma doses in the range of 10Gy - 1KGy. Figure 4 shows the dose response

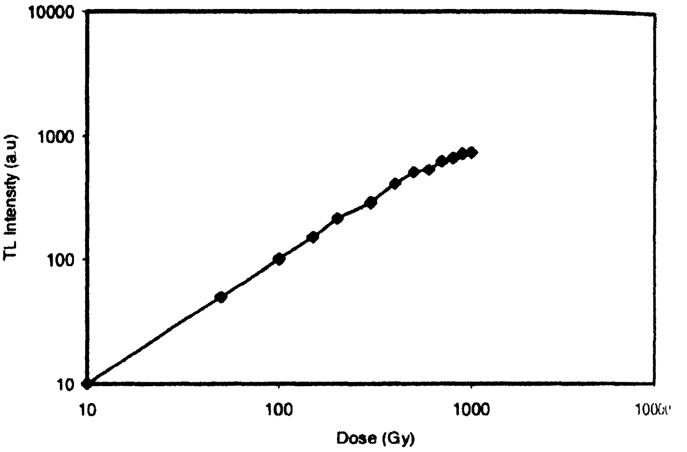

Figure 4. Dose response curve of the quartz of 150°C TSL peak

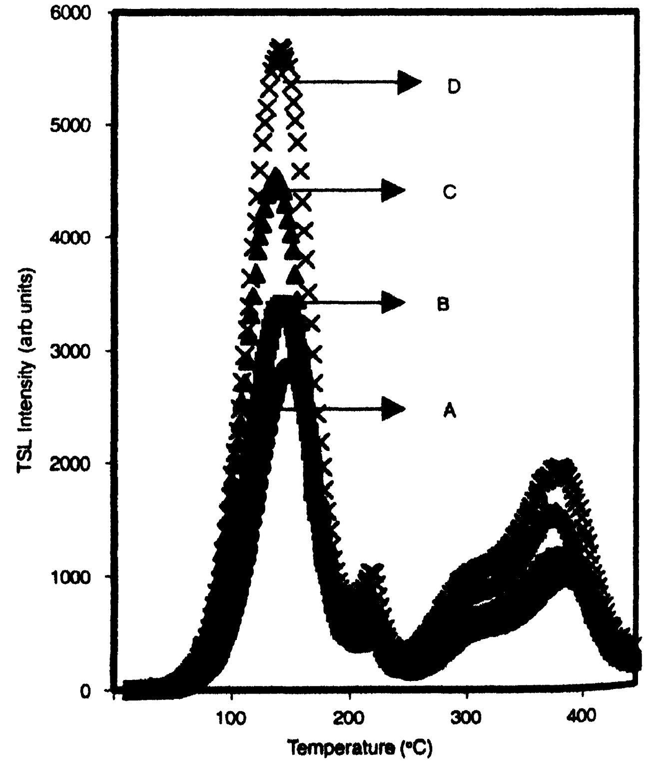

Figure 5. The glow curve of quartz treated with different gamma doses (A) 50Gy, (B) 75Gy, (C) 100Gy and (D) 120Gy.

curve of the 150°C TSL peak of granitic quartz. The dose response is linear in the lower dose levels and at the same time, the saturation trend occurs at the higher dose level. The same trend follows in all other samples. Figure 5 shows the glow curve of granitic quartz sample irradiated with different gamma doses. A systematic shifting of T_m towards the lower temperature side with increase of gamma dose is observed. All the samples followed the same trend, but at very high dose (860Gy) only, the low temperature peak (150°C) is shifted towards low temperature side (see Figure 5). The peak maxima gets shifted towards the lower temperature side with increase in the radiation dose and this is a clear evidence of the second order kinetics [14,15]. This result exactly matches with the preliminary evaluation of the previous method as discussed. This confirms that the samples need higher dosage to act as best luminescent substances [2].

4. Conclusion

The quartz samples studied in the present work were separated from natural granite. The present study highlights only the preheat treatment. Above 800°C, rapid increase in sensitivity upto 900°C was observed and after 900°C, it decreased suddenly due to reduction in trap population. Since the trap population could be expressed as a function of received radiation dose, the total dose is estimated when the minimum level, present level and the increase per unit dose are known. According to Han *et al* [2], sensitivity increases 10^4 times for 1 hr annealing at ~1000°C. But the present study shows an increase of about 10^5 times for annealing at 900°C itself. The initial concentration and decay rate of the traps can be used to estimate the cooling age since the granitic quartz last cooled to 200°C. Radiation sensitive traps are very stable for temperature lower than 200°C. 1hr annealing at 400°C, resulted in a decrease in sensitivity indicating that the radiation sensitive traps are destroyed. The present results evidenced that the annealing treatment at 900°C for 10hr is the optimum condition for TSL sensitization of granitic quartz using rapid cooling. The change in TSL sensitivity after annealing is explained on the basis of trap creation and destruction mechanism. The 150°C peak has been found to obey second order kinetics.

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