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Spurious and regenerated thermoluminescence from natural calcite crystals

V Ponnusamy, V Ramasamy*, M Dheenathayalu and M Gopalakrishnan

Department of Physics, Annamalai University, Annamalainagar-608 002, India

E-mail : srsaranram@rediffmail.com

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Abstract : In the present investigation, the thermostimulated luminescence (TSL) method is employed to study the geologically important ten-calcite crystals which were collected from Thalaiyuthu mines, Tirunelveli district, one of the Southern most district of Tamil Nadu, India. The natural thermoluminescence (NTL) glow curve shows the peaks at 260°C and 345°C. In addition to these two peaks, a new peak is appeared at 140°C after irradiation. There is an increase in intensity without change in position and shape of these three peaks when annealed at 400°C. The observation of the spurious thermoluminescence (TL) signal is found to be very different from the other trapping centers. The regenerated thermoluminescence (RTL) equals the intensity of original NTL (345°C) signal during 10th day measurement. After 10th day, there is saturation in intensity.

Keywords : Spurious TL, regenerated TL, natural TL, calcite

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1. Introduction

Thermostimulated luminescence (TSL) is one of the active fields of research and its application in radiation dosimetry and geological or archaeological dating continues to attract worldwide attention of researchers. Most commonly, naturally occurring minerals possess a property of TSL emission. Among these, quartz, calcite and fluorite are the most studied minerals because of their excellent TSL sensitivity. Calcites are commonly widespread mineral on the earth as a main constituent of limestone, speleothem, coral *etc.* Calcites are mainly used in cement, paint and in chemical industries and to control pollution from all types of industrial wastes. Calcites normally incorporate various impurities (Pb,Mn,Cu,Co,Mg,Fe, *etc.*) during crystallization. TSL glow curves and the emission spectra of calcite have been the subject of numerous studies due to the geological and archaeological importance of this mineral [1-12]. A careful sample preparation and heat treatment of the samples are the essential factors for the accurate determination of the age of the sample. Two factors which can be detrimental to such age determinations are the presence of spurious TL and regenerated TL signals [13,14]. Very few detailed and significant investigations on this aspect of calcite were attempted so far. In the present work, the behaviour of spurious and regenerated TL for natural calcite crystals are investigated.

* Corresponding Author

2. Materials and methods

In the present investigation, the TSL method is employed to study the geologically important calcite crystals which were collected from Thalaiyuthu mines, Tirunelveli district which is one of the geological important Southern most district of Tamil Nadu, India. The location of the study area is shown in Figure 1. Thalaiyuthu is located about a distance of 6 km North of Tirunelveli and 5 km from South of Nanjakulam. The study area lies between latitude of 77°43′ East and longitude of 8°47′30″ North falls in the toposheet number 58H/9. About 10 crystals were collected at different locations from the mines. The crystals were stored in dark until the TSL measurements were carried out. 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. The magnetic particles are removed using a suitable magnet so that to improve the emission of TSL signals.

The natural thermoluminesce (NTL) measurements were carried out for all the ten natural calcite crystals. Then the samples were annealed in air at the temperature of 400°C for 1hr and then rapidly cooled in air. The annealed samples were irradiated by using ^{60}Co gamma source with a dose rate of 680Gy/

hr and the TSL measurement were carried out by using Nucleonix TLD-96 reader at the heating rate of 10°C/sec. The TSL glow curves were recorded immediately after irradiation to avoid loss due to fading. The data were collected from computer after subtraction of black body radiation.

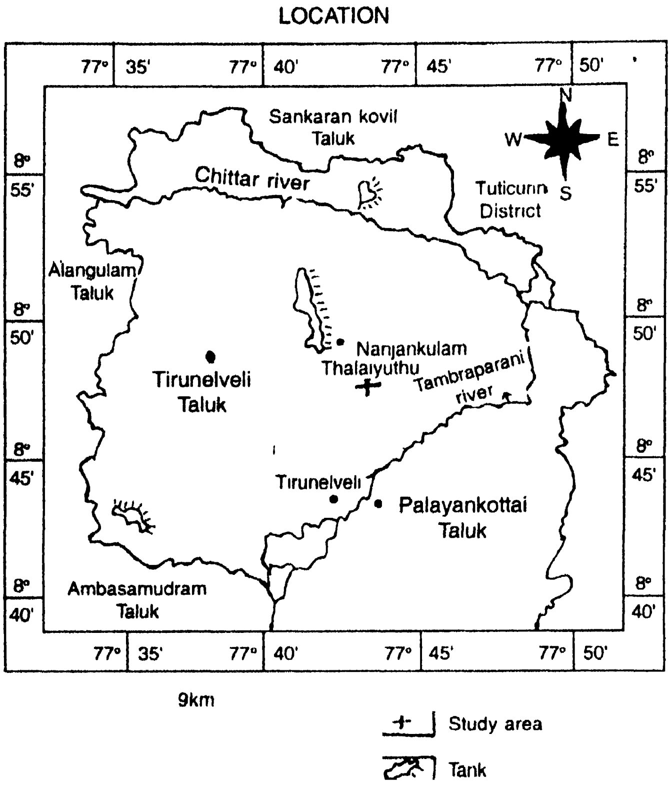

Figure 1. The location of the Tirunelveli district – Study area (Thalaiyuthu).

3. Results and discussion

3.1. Glow curve characteristics :

The NTL measurements are recorded for all the ten samples. The glow curves obtained for all these samples show similar structure in respect of shape, intensity and peak position. A representative glow curve characteristics of natural, natural plus irradiation induced TSL and together with annealed sample glow curve is illustrated in Figure 2. It is observed that the natural thermoluminescence (NTL) of the sample consists of two high temperature glow peaks appearing at 260°C and 345°C ('a' in Figure 2). When the sample is irradiated by using ^{60}Co-gamma source in the dose level of 150Gy, it shows a new peak at 140°C. At the same time, the NTL peak at 260°C is found shifted to 255°C with increasing in intensity and there is no change in the peak position of 345°C but with slight enhancement in intensity ('b' in Figure 2). Above this dose level, there is no response from 345°C NTL peak. According to Lewis [15], the peak at around 300°C is caused only due to lattice defect and not by any other impurity content and hence the enhancement in intensity at 345°C may be attributed to the cause of lattice defects. The other two glow peaks (140°C and 255°C) enhance in intensity systematically with the dose level.

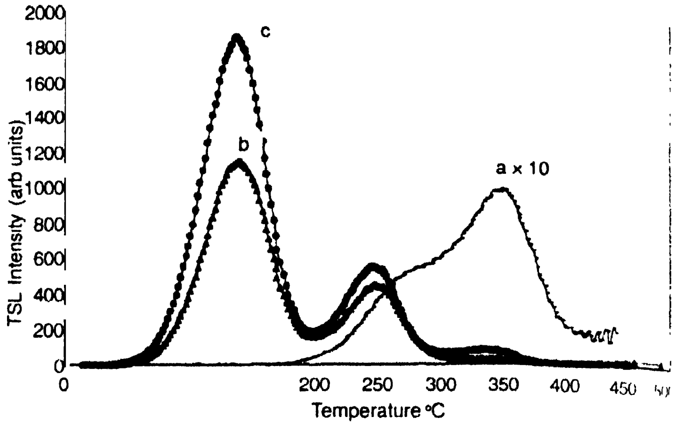

Figure 2. Thermostimulated luminescence of natural blue colour calcite a) Natural thermoluminescence (NTL) b) NTL+Dose (150Gy) c) annealed at 400°C for 1hr.

Then the sample is annealed at 400°C for 1hr, which shows the same three glow peaks as that of 150Gy and there is no change in position and shape of the glow curve except the increase in intensity ('c' in Figure 2). It is observed that the low temperature glow peak (140°C) is predominant over the higher temperature peak at 255°C. Generally, it is a well known fact that in the TSL of $CaCO_3$ the low temperature peak is intense relative to all other peaks if the manganese content is high [16].

When the sample is irradiated with increased dose levels the peaks at 140°C, 255°C and 345°C are observed. But when the sample is irradiated after annealing, the intensity of the above peaks increases without any change in peak position and shape. This may be due to the increase in the number of traps into the lattice.

3.2. Spurious TL :

When a phosphor is heated above certain temperature, typically 400-500°C, all the trapped electrons and holes, constituting the peaks at lower temperatures, will be trained. Normally, in successive heating, only the black body radiation or thermal radiation appears. However, most of the thermoluminescent materials produce the so called 'spurious TL' or 'regenerated TL' [17,18]. This type of non-radiation induced TL has not been observed in calcite [19]. Aliquots of the natural calcite crystals were heated to 450°C in order to measure their natural TL. During TL glow measurements of calcite crystals, it is observed that after the first glow, each calcite crystals produced TL around 345°C if they were heated again. The natural TL signals of all the samples are similar in peak position and shape (see Figure 3). Pagonis *et al* [20] have studied three different types of calcites at different origin and they observed the similar natural TL signals.

Earlier, different types of spurious TL signal have been identified as (a) chemiluminescence produced by surface oxidation during TL readout, (b) charge transfer from deeper traps due to light exposure and (c) triboluminescence due to grinding [18]. With the view of Wintle [13], Ninagawa *et al* [14], this type of spurious signal can be reduced or even eliminated by etching the powder surface with weak acids and by using an inert atmosphere during TL readout. In the present investigation, the same type of measurement in two different atmospheres such as air and nitrogen (inert), shows no significant change in the observation of spurious TL signal. From these results, we can suggest that it is not due to chemiluminescence produced by surface oxidation during TL readout. The elimination of this TL signal by using etching procedure is also failed in this study. The results obtained by Pagonis *et al* [20] supports the present investigation. They observed that the spurious TL exhibited by the samples is a residual form of triboluminescence and/or chemiluminescence in calcite which could not be eliminated by the usual etching /inert atmosphere procedures.

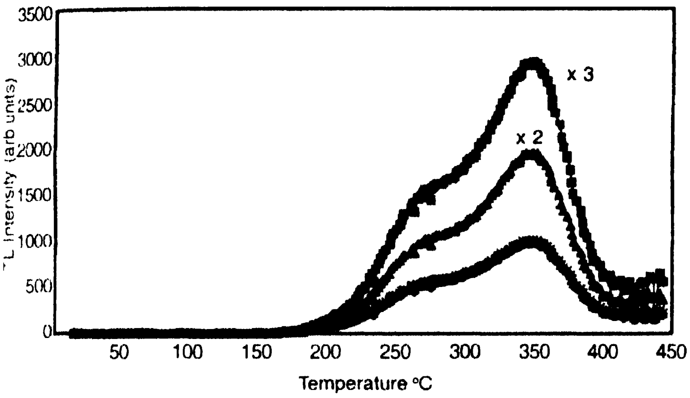

Figure 3. The natural TL glow peaks of natural calcite samples (for clarity only four samples are shown) of different sites of Thalaiyuthu mines, Tamil Nadu, India

The observation of this spurious TL signal is found to be very different from other trapping centers which can be filled with ionizing radiation. The traps associated with this spurious signal, exhibit a regeneration effect on the TL explained as follows.

3.3. *Regenerated thermoluminescence(RTL) :*

The samples were heated twice to 450°C in order to measure their natural TL and corresponding black body radiation. After the TL readout, the sample is then stored for fifteen days at room temperature (RT) in the dark, to avoid any effect due to light and radioactive sources. The periodical measurements of both black body radiation and the enhancement in TL signals are carried out for a span of 15 days. It is observed that in the first span of 10 days, there is a virtual enhancement of intensity and in the last five days, a saturation in intensity (Figure 4). In the tenth day, the intensity of regenerated thermo luminescence (RTL) signal becomes equal to the original NTL (345°C) signal. According to Pagonis *et al* [20], the RTL signal starts regenerating within a period of few hours after the TL readout and reaches saturation within two weeks. After reaching saturation, RTL signals for all the calcites remain constant for all the observation period at least one month.

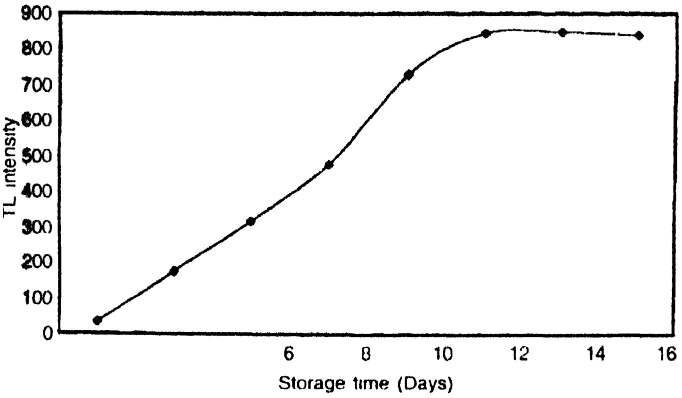

Figure 4. The regenerated thermoluminescence characteristics of 345° C peak in calcite sample

From this investigation, it is observed that all the samples showed a regenerated TL signal around 345°C and the behaviour of this peak is found to be very different from other trapping centers which can be filled with radiation. It is also noticed that the intensity of this regenerated signal, depends on the storage time and annealing temperature. Elimination of this peak was found by annealing at 600°C for 5hr. From this result, the TSL peak at 345°C or above 300°C is found to be non-radiation induced peaks and it does not interfere with radiation-sensitive low temperature TL peaks.

3.4 *Kinetics of RTL signal :*

In order to obtain the kinetic parameters of the RTL peak, the well known initial rise and Chen's peak shape methods are used with the help of the data in Figure 3. From these two methods, it is observed that a trap depth energy (E) 0.55 eV indicates the first order kinetics. With the help of the theoretical expression, one can calculate the corresponding frequency parameter 's' from

$$(E/kT^*).\exp(E/kT^*) = s.T^*/\beta,$$

where T* is the temperature of maximum TL signal, β is the heating rate and k is the Boltzmann constant [18]. The values of s obtained from the above expression show a half life of 5-10 min at room temperature (RT) for the RTL peak examined.

4. Conclusion

Previously, various dosimetric crystals have been studied for the phenomenon of RTL signal [17]. According to them, the RTL signal depends on factors like storage time, pre-dose effect, storage temperature and heat treatment of the sample. They explained their results by assuming a triplet defect consisting of an electron, a trap and a slowly moving defect in the form of a free radical. Pagonis *et al* [20] have also reported that the same mechanism is responsible for the RTL phenomena in calcite. The present investigation show a RTL signal around 345°C and the intensity of RTL signal becomes equal to the original NTL signal after a 10th day measurement. The behaviour of this particular peak is different from other trapping centers that can be filled with radiation. In the present study, the intensity of the RTL signal mainly depends on the storage time and annealing temperature as observed in the earlier work. The particular peak at 345°C gets eliminated at 600°C for an annealing time of 5hr. Hence, it can be concluded that the peak at 345°C to be non-radiation induced peak, which is due to lattice defect, since there is no observation of enhancement of this peak after a dose level of 150Gy. At the same time, it does not interfere with radiation sensitive low temperature TL peaks.

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