110°C thermoluminescence glow peak of quartz – A brief review

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Abstract. The 110°C glow peak of quartz, though unstable at room temperature, has worked wonderfully in archaeology and retrospective dosimetry due to its pre-dose sensitization property. Various aspects of the peak, like its nature, defect centres involved, the impact of different stimuli and its application have been extensively studied. The main aims of this review are to (i) summarize briefly the work carried out on the various facets of this TL glow peak during the last four decades and (ii) identify the areas which need further attention in order to have a better understanding of the luminescence characteristics of this TL peak.

Keywords. Thermoluminescence; quartz; 110°C thermoluminescence peak; pre-dose.

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1. Introduction

Quartz, the most abundant mineral on Earth, is present in most of the samples useful in luminescence studies. It demonstrates excellent luminescence properties; sensitivity, reliability, versatility and compatibility with the detection system. Its thermoluminescence (TL) properties are quite diverse in nature and depend strongly on its origin and region from which it is derived [1–4]. Though glow curves vary from sample to sample, the typical glow peaks of quartz above the room temperature are centred around 110, 230, 325 and 375°C (figure 1) [5,6]. The TL emission has been, generally, observed to be centred around 370, 470 and 620 nm [7–10]. The physical conditions prevailing during the formation of quartz has a lot of bearing on its emission characteristics [11–13]. The quartz derived from volcanic ash layer, containing β-quartz, has been observed to be rich in red TL, while the one derived from pegmatite and granite strata yielded a typical blue TL [11]. Each spectral emission has been associated with different recombination centres employing the de-localized band model [14].
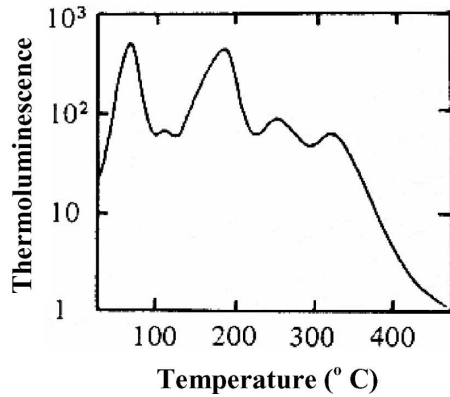
Figure 1. Typical TL glow curve of natural pink quartz after administering a radiation dose of 2.5×10^3 Gy and measuring the TL at a heating rate of $25°C$ min^{-1} [6].

The $110°C$ peak of quartz having a half-life of a couple of hours at room temperature was of no use in any of the application until its sensitization after a combined treatment of radiation and heat, the so-called pre-dose sensitization, was observed [15]. Zimmerman proposed a phenomenological model, based on the transfer of charge from one recombination centre to another, which explained most of the characteristics of the pre-dose sensitization process [16]. The pre-dose sensitization mechanism involves the integrated administration of radiation and heat treatments. The sensitivity of the crystalline quartz, in this case, is governed by the previous radiation dose experienced by it at room temperature and the subsequent thermal activation. This charge transfer from one recombination centre to another was proposed to enhance the recombination rate due to increased population of holes trapped in the recombination center and decreased competition from other trapped holes. The various features of the Zimmerman model have remained valid till date though certain minor modifications had to be introduced in order to take into account some phenomena not addressed by this model. Attempts were, also, made to explain the pre-dose sensitization phenomenon on the basis of phase transition and creation of the corresponding characteristic hole traps [17]. Annealing the quartz beyond the inversion temperature, α to β transition, was presumed to create new hole centre L$'$ similar to the centre responsible for $110°C$ TL peak, the L centre. But, this model could not explain different phenomena observed in the pre-dose sensitization process.

Though quartz has been the extensively studied natural mineral, it is the effective utilization of this low-temperature, $110°C$, glow peak of quartz that has attracted considerable interest in particular. Studies have been undertaken to (a) understand the nature of this peak in both natural and synthetic quartz, (b) identify the centres involved in the luminescence process, (c) study its response to thermal and radiation treatments, (d) its correlation with the OSL emission and (e) eventually, evolve models to explain all the observed characteristics of this glow peak [18–23]. The impact of heat and radiation treatment on the TL properties of the $110°C$ peak has been addressed by various workers [5,24–29]. The main phenomena studied

were: (i) variation in TL sensitivity, (ii) behaviour of the growth curve, (iii) role of deep traps and (iv) change in the spectral emission. These treatments have been observed to have a strong influence on the luminescence behaviour of the 110°C peak. The general observations reported by various workers are: (i) sensitization of the glow peak, (ii) shifting of the peak positions, (iii) generation of new peaks and (iv) variation in emission spectrum.

A workable TL peak at a temperature as low as 110°C is a big advantage in TL measurements, as the unwanted effects due to heating at higher temperatures can be avoided. These include (i) black-body background radiation, (ii) thermal quenching and (iii) heat-induced chemical reaction in the specimen. The modus operandi involved in the procedures based on the pre-dose mechanism is to monitor the increase in the sensitization rather than the conventional accumulation of TL. This mode of measurement has been effectively utilized in various applications: (i) archaeological dating, (ii) retrospective dosimetry, (iii) authenticity testing, (iv) firing temperature measurements etc. [30–35]. This method has been found to have a great potential in the estimation of the low equivalent dose (paleo-dose) in the range of ∼mGy to a few Gy. The upper limit is set by the early onset of saturation, at around several grays. The conventional method has been observed to have limitations in this dose range due to poor TL intensity at such doses coupled with the various unwanted effects generated by heating at higher temperatures, as listed above.

The correlation of the 110°C glow peak with optically stimulated luminescence (OSL), a very powerful analytical method, reported by various workers, has enhanced the importance of this peak [22,36,37]. As a result of this correlation, it has been routinely used to monitor the sensitivity change occurring in the OSL measurements due to pre-heat, involved in the protocol. It is now widely accepted that the two luminescence phenomena share the same centres [38,39].

A lot of literature is available on the luminescence properties of the 110°C glow peak of quartz. The characteristics of the pre-dose mechanism have been analysed in detail so as to render reliability to the pre-dose technique. The intricacies involved in the pre-dose measurements have been reviewed by Bailiff [31]. During the last two decades a lot of work has been carried out to understand the nature of this first glow peak of quartz in general and its pre-dose phenomenon in particular. The motivation behind this paper has been to update various facets of this peak. The emphasis has been to take a look at: (a) nature of defects involved in the TL process, (b) the models developed to explain various phenomena exhibited by this glow peak, (c) impact of radiation and thermal treatments on its luminescence properties and (d) the correlation of this glow peak with the OSL emission of quartz. An attempt has also been made to identify the areas that need a re-look for better understanding of the various aspects of this TL glow peak.

2. Nature of the 110°C peak

The behaviour of the 110°C glow peak, like other glow peaks of quartz, is quite diverse in nature and depends strongly on the nature of the sample. The actual position of the peak is generally within the range 90–120°C (heating at 5°C s^{-1}),

but, for all practical purposes it is referred to as the 110°C glow peak [40]. Though it appears as a nice smooth single peak with a small hump at the lower temperature end, it actually consists of a number of overlapping glow peaks. Experiments were conducted to unveil these glow peaks in synthetic quartz crystals using various irradiation temperatures (273–293 K). The glow curve obtained after irradiation at different temperatures in this range was observed to unfold the 110°C glow peak into three overlapping peaks [23]. The difference in the sensitization behaviour of these individual peaks suggested that the centre(s) responsible for the 110°C glow peak might have an internal structure.

The luminescence emission spectrum of 110°C peak has been recorded by a number of workers. The most frequently observed bands are centred around 360–380 nm, 420 nm and 450–470 nm. But, emission at ∼550 nm and 610 nm (red TL) have also been reported [24,41,42]. Various properties of 110°C peak, like (i) degree of saturation and (ii) thermal activation characteristics has been observed to vary significantly in various emission bands. The variation in the thermal activation characteristics suggested different sensitization mechanisms operating in various emission windows [42]. The growth curves of the 550 nm emission were found to saturate at around a dose of one order higher than in case of the conventional emission band of 360 nm. The red emission signal of quartz has also been incorporated for dating by various researchers [43,44].

A variety of defect centres are known to exist in quartz; aluminium associated centres, oxygen-vacancy centres, germanium associated centres, H-atoms etc. [45,46]. Based on ESR, IR and luminescence measurements it is now widely believed that the traps responsible for this peak are the $(GeO_4)^-$ electron traps and the centres $(AlO_4)°$ and $(H_3O_4)°$ act as recombination centres. The effectiveness of these recombination centres differs between virgin and stimuli-treated specimen. The similarity in the TL behaviour of the synthetic and natural quartz made Petrov and Bailiff [23] to believe that defects associated with the intrinsic SiO_2 lattice have a role in the sensitization process. This stems from the fact that the synthetic quartz specimen contains fewer impurities than the natural one.

The exact contribution of various proposed centres to the luminescence process in the case of the 110°C glow peak of quartz seems to be far from over. Various studies have revealed the complicated character of these centres. Though correlation of the various emission windows with the corresponding centres has been attempted, a generalized formalism has yet to be established. A better understanding of the role of intrinsic and extrinsic centres will be useful in this direction. Do one or more than one centres contribute and what are their degrees of contributions in luminescence process of quartz from various regions and origins needs to be addressed. The detailed characterization of the 110°C TL peak in the different emission windows will also be useful to get a better feel of the centres involved in the luminescence process.

3. Impact of heat treatment

The impact of heat treatment on the TL properties of the 110°C peak has been studied extensively and various important features reported are as follows:
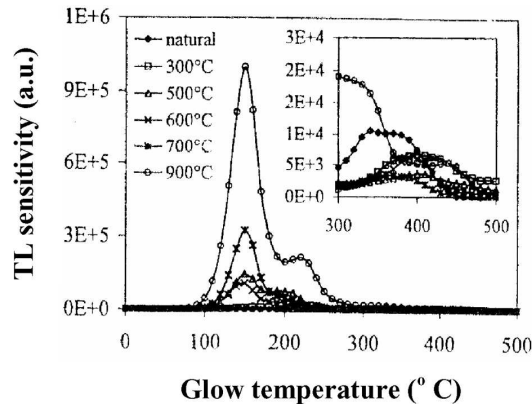
Figure 2. TL intensity at different heating temperatures [27]. Inserted plot depicts the same TL sensitivities from 300 to 500°C. The sensitization initiates at ∼200°C and continues up to 900°C. The impact of sensitization is prominent in the case of 110°C TL peak only [27].

3.1 *Sensitization*

Thermal history of the quartz specimen, which includes (i) firing temperature, (ii) duration of firing, (iii) cooling rate and (iv) environment prevailing during firing episode, has been found to have a lot of bearing on the luminescence characteristics of the 110°C TL peak [25,47,48]. The TL sensitivity of quartz, both natural and synthetic, has been observed to be strongly influenced by the heating temperature during firing episode. This sensitization is due to pure thermal treatment and should not be confused with the pre-dose effect. The sensitization with firing has been, generally, observed to initiate at ∼200°C and saturates at ∼1000°C. An enhancement as high as ∼10^5 has been recorded after a firing of 900°C (figure 2) [27]. Apart from this enhancement in sensitivity, the growth curve of the 110°C peak has also been observed to get modified by the firing temperature. The degree of superlinearity was observed to reduce with increase in the firing temperature and, eventually, gets completely removed after the firing temperature of 900°C [29,47,49] (figure 3).

The phenomenon of sensitization with firing has been explained on the basis of the change in the competition among various centres during TL read out, i.e. heating stage [49,50]. All forms of quartz, natural or synthetic, contain aluminium, substituting for silicon in the lattice. The monovalent charge compensators, including Li^+, Na^+, H^+ are always present as interstitial ions. These interstitials play a big role in the kinetics of various centres present in quartz. In as-grown state the monovalent alkali ions act as charge compensators for Al^{3+} ions, but irradiation at room temperature drifts the alkali ion to the centres, which are pre-cursors to the E'_1-centres. Firing, i.e. annealing at higher temperature, allows these ions to return back to the as-grown configuration which, eventually, reduces E'_1-centre concentration. It is the reduction in these centres, named as deep traps, with firing which have been reported to be responsible for these phenomena of sensitization
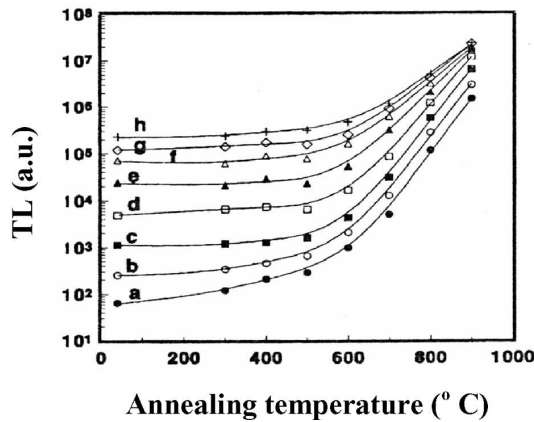
Figure 3. TL sensitivity as a function of annealing for various doses. (**a**) 3 Gy, (**b**) 5.5 Gy, (**c**) 11 Gy, (**d**) 22 Gy, (**e**) 38 Gy, (**f**) 60 Gy, (**g**) 81 Gy and (**h**) 120 Gy. The superlinearity in the sensitization reduces with the increase in the firing temperature [47].

and removal of non-linearity in the case of the 110°C TL peak [51–53]. The annealing characteristics of E_1'-centre seems to makes it a strong contender for being the competitor. The formation of this centre has been found to have a direct correlation with the presence of alkali ions present in the lattice [50].

Studies carried out to monitor the variation in sensitivity of both the 110°C TL and fast component of the CW-OSL emissions with firing at various high temperatures have also been observed to be affected by the phase transitions. The enhancement has been reported to be large, in particular, around heating temperatures of ∼800–900°C (figure 4), the region of quartz-2 tridymite phase transition [25,54–56]. Based on various techniques TL, LM-OSL, EPR and CW-OSL it has been reported that UV emission (360 nm) was enhanced by heating to 700°C whereas the 1060°C heating enhanced the red emission (630 nm) [54,57]. This suggests that sensitization curves also seem to carry the signatures of the phase transition.

There is no general formalism that can exactly explain and predict the behaviour of the luminescence characteristics of 110°C glow peak of quartz with heat treatment. Samples derived from various regions do not behave in an exactly similar way as far as their mode and degree of sensitization is concerned. Apparently, this may be primarily due to variation (i) in the nature of impurities present in their lattice, (ii) in the thermal history experienced by the specimen during their formation or thereafter and (iii) in the dominant mode of sensitization, which can occur due to annihilation of the competitor or phase transition. The removal of the competitor during firing seems to be more or less an established phenomenon. But, the situations where the role of phase transitions rather than that of the competitor become dominant need to be understood in a much better way. May be it has to do something with the provenance of the specimen?
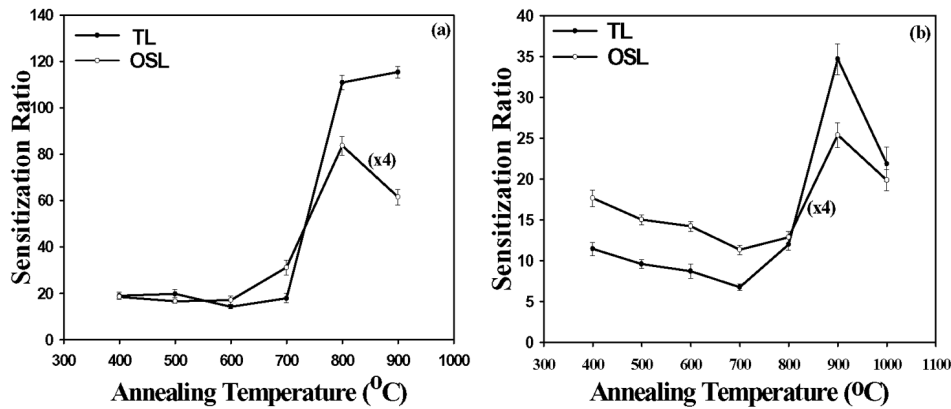
Figure 4. Measurement of the TL sensitization of the Thar and Sludge samples after refiring at various high temperatures, 400–900°C in the case of Thar and 400–1000°C in the case of Sludge, in steps of 100°C. The pre-dose treatment consisted of test dose of 0.4 Gy, pre-dose of 10 Gy and thermal activation temperature of 500°C. The arrows point out the firing temperatures experienced by the specimen prior to refiring, 600 and 800°C in case of Thar and Sludge respectively [56].

3.2 *Emission spectrum*

The un-annealed quartz samples on irradiation have been observed to yield an emission band of the 110°C peak that prominently spreads from 420 to 520 nm, centred at 470 nm. But, the thermal treatment has been found to generate a new emission band, centred at ∼370 nm [54,58]. It is this component which has been observed to get sensitized by thermal treatment, while the 470 nm component was found not to participate in this phenomenon. The 370 nm component has been observed to have a direct correlation with the firing temperature, increasing sharply with temperature as is evident from figure 5 [59].

The thermal sensitization of the 110°C peak has been reported to have no correlation with $(AlO_4)°$ centres, the centres responsible for the 470 nm emission [60]. The studies based on ESR data, on the other hand, demonstrated the production of $(H_3O_4)°$ centres, the centres responsible for 370 nm emission after the firing episode. Sweeping, the process of electro-diffusion of monovalent ions into quartz lattice by application of an electric current at high temperature, H^+ ions into quartz also confirmed the significant role of H^+ in the sensitization process. This process produced results qualitatively similar to those induced by firing quartz [61]. The $(H_3O_4)°$ centre is similar to $(AlO_4)°$ centre except that Si^{4+} is replaced by three protons. The annealing properties of both these centres have been observed to be quite similar [62] (figure 6). It essentially means that the same annealing mechanism may be operative for these two defects. All these studies inferred that the $(H_3O_4)°$ seems to be the centre responsible for the TL emission at 380 nm.
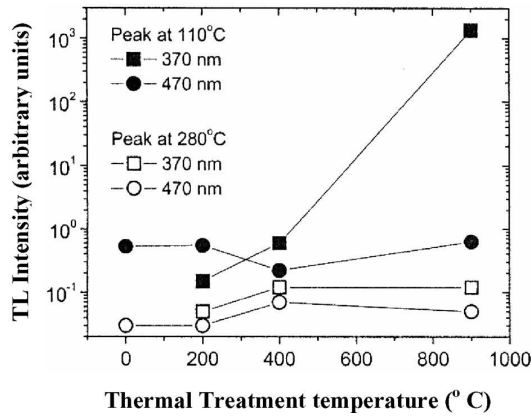
Figure 5. TL emission as a function of annealing temperature during thermal treatment. The heat treatment sensitizes the 370 nm emission component while the 470 nm component does not seem to participate. Again, it is the TL peak at 110°C which has a dominant role in the entire process [59].
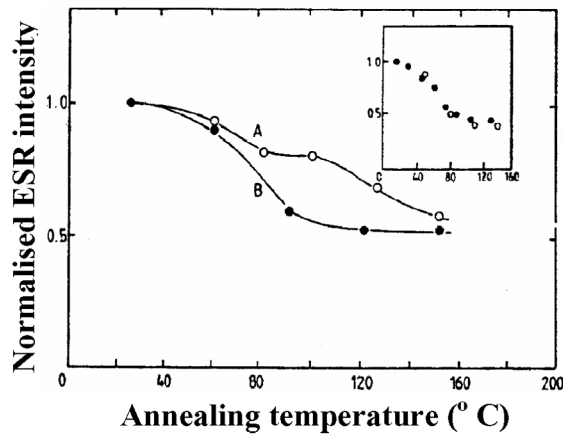

Figure 6. Pulse annealing curves of $(H_3O_4)^\circ$ centres in EGX quartz; A – received sample and B – a fired sample. Inset depicts the similarity between the annealing profiles of the $(AlO_4)^\circ$ (filled circles) and $(H_3O_4)^\circ$ centres (empty circles) [62].

4. Pre-dose phenomenon

The various features of the pre-dose sensitization of the 110°C peak of quartz are described as follows:

4.1 *Zimmerman's model*

The model is based on two electron traps; one corresponding to the 110°C peak, T, and the second, S, incorporated for charge neutrality; and two hole traps, one
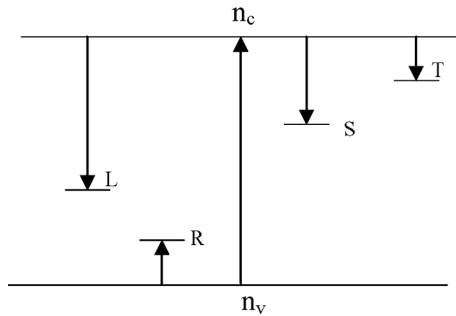
Figure 7. The energy level diagram of Zimmerman's pre-dose model. T, L, S and R represent the electron trap, recombination centre, deep trap and hole reservoir respectively [16].
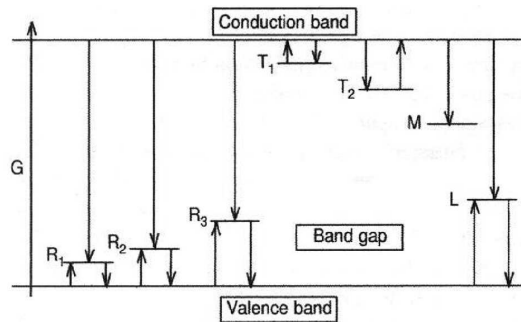

Figure 8. Model incorporating more than one reservoir centres in order to explain various features of the luminescence in the case of $110°$C glow peak of quartz. T_1, T_2 and M are electron centres. R_1, R_2 and R_3 represent reservoir hole traps and L the luminescence centre [63].

acts as a luminescent centre for $110°$C peak, L, and the other behaves as a reservoir centre, R (figure 7) [16]. The main hypotheses governing the pre-dose phenomenon are: (i) pre-dose (paleo-dose in the case of natural samples) essentially populates the R centres, (ii) heating at around $500°$C transfers holes from R to L centres and (iii) the probability of the radioactive recombination for the electrons released from L traps during TL read out enhances considerably, due to the increase in the availability of recombination centres, L.

The Zimmerman's model is still on a firm ground except for some minor modifications. Attempts have been made by various researchers to model various features of the luminescence observed in quartz [40,63–67]. Chen had to introduce another competing electron trapping centre in order to explain the linear dependence of the TL peak on both the test dose and pre-dose [64]. The presence of these competitors was, again, found necessary in order to explain the presence of non-linearity in the TL behaviour of unfired quartz as compared to linear TL growth in the case of fired specimen. So, the centre S in figure 7, which was incorporated by Zimmerman in her model for charge balance, has been suggested to play the role of a competitor during the heating stage of the TL process. Subsequently, these competitors were

reported to be the E_1'-centre, the same centres involved in thermal sensitization of the $110°C$ TL peak, as reported in §3. Chen and Leung [66] were able to successfully simulate the pre-dose effect and the sequence of steps involved in the pre-dose dating procedure by adopting modified Zimmerman's model, two electron and two hole centre model [66]. It is the role of the S centre which differentiates it from the Zimmerman's model.

The process of evolving numerical models for the pre-dose sensitization continued, essentially, to take into account various phenomena, like the thermal activation characteristics (TAC), isothermal sensitization, the nature of TAC for different values of pre-dose and dose quenching. The nature of the thermal activation curve (TAC), essentially, reflects the distribution in activation energy of the reservoir traps, R. As the activation temperature is increased more and more holes get transferred from R to L centres. Experiments involving the isothermal activation and progressive thermal sensitization measurements were performed to understand the nature of the thermal activation curve [40]. The former involves measurement of the sensitivity change happening during the heating of a sample at a constant temperature for extended periods of time, while the latter measures a series of isothermal sensitization for the same aliquot at increasing activation temperature.

As the release of holes from R-centre is governed by the Arrhenius law, the transfer of charges will depend on the heating temperature and the TAC should have been ideally represented by a single saturating exponential. But, the TACs obtained in the isothermal sensitization measurements could not be fitted with such exponentials [40,63]. This led to the formalism of multi R-centres, i.e., more than one reservoir centres are operational in the pre-dose mechanism. Therefore, the progressive thermal sensitization experiments were conducted to understand the feasibility of incorporating more than one R-centre in the luminescence mechanism. The results indicated the pattern of sensitization to be complex in nature. A multiphase sensitization behaviour with increasing heating temperatures was observed. To a large extent, this upheld the hypothesis of multi-R-centre configurations. Based on these findings a modified Zimmerman's model consisting of multireservoir hole traps were developed (figure 8) [40,63]. These models were found to be able to reproduce various empirical results by means of numerical simulations. The proposed reservoir centres have been suggested to get activated at different activation temperatures during the thermal activation process.

Though, over a period of time, more than one reservoir has been incorporated to take into account various features of the pre-dose process the exact nature of these centres and their precise contribution to the pre-dose sensitization needs further scrutiny. It is worthwhile to take into account the role of thermal treatment apart from its contribution in transferring charge from one centre to the other in the pre-dose process. A comparative analysis of thermal and pre-dose sensitization makes one to believe that the heating involved in pre-dose protocol can, in principle, also introduce some thermal sensitization apart from its conventional role of transferring the charges. On the other hand, heating at $\sim500°C$, the thermal activation temperature used in the pre-dose phenomenon, has been reported to generate some kind of de-sensitization effect. The argument behind this hypothesis is that the traps corresponding to other glow curves of the quartz which appear in this temperature range, like $\sim230°C$ and $375°C$, may get emptied during heating

at this temperature. Subsequently, this may enhance the competition experienced by the centres responsible for the 110°C TL peak during the TL read out [29]. The role of thermal treatment in the pre-dose procedure needs a better understanding *vis-à-vis* the effects it can generate in the luminescence process, as described above. Does the composite influence of these transformations brought out by this thermal activation make it difficult to represent the TAC by single saturating exponential? This possibility may eliminate the need to have more than one reservoir centres in the models representing pre-dose process.

4.2 *Sensitization characteristics*

The sensitization, as discussed earlier, is dependent on the pre-dose, activation temperature and the test dose utilized in pre-dose treatment. It is worthwhile to mention here that, apart from these parameters, the pre-dose behaviour also depends on the nature of the quartz specimen [67]. The thermal activation initiates at ∼200°C, peaks typically at ∼500°C and reduces appreciably thereafter, but, can be sustained up to 700°C [31]. The thermal activation characteristics varies from sample to sample. The growth curve saturates at a very low radiation dose, essentially due to saturation of R-centres after a few Gy.

The movement of hydrogen in the quartz lattice during irradiation and annealing has been reported [60]. It has been postulated that these atoms get unlocked during irradiation and heating generates mobility in them. During diffusion in the lattice they get trapped at centres which are precursors to $(H_3O_4)°$ centres. It is these centres which have been proposed to participate, while $(AlO_4)°$ centres remain more or less ineffective in the sensitization process. The scenario here seems to be similar to the one operating during thermal sensitization, as discussed in §3.2. This has been confirmed by observing the enhancement in the TL emission which has been again observed to be centred at around 370 nm whereas the 470 nm component remained unaltered. But, as mentioned already, role of intrinsic defects of SiO_2, i.e. oxygen defects, cannot be overlooked here [23].

5. Applications

A workable TL peak at a temperature as low as 110°C is the best thing a TL worker could have asked for as operating at this range of temperature removes the phenomena that generally deteriorate the TL signal, like background black body radiation, heat-related chemical changes in the sample and thermal quenching. This special feature has rendered it one of the cleanest workable peak in TL studies. But, in order to ensure the reliability of the technique, various assumptions in the protocol must be looked into carefully. These include (i) nature of the thermal activation curve, (ii) the variation in the sensitization process during antiquity since last firing, (iii) behaviour of the thermal activation with applied radiation dose and (iv) the degree of dose quenching. Depending on the nature of these findings a suitable method based on the pre-dose technique must be identified for

the equivalent dose measurement. The technique has been exploited extensively in the applications described below.

5.1 *Dosimetry*

The introduction of quartz grains for low-level dosimetery has been found quite effective in radiation accident dosimetry, known as retrospective dosimetry [30,68–71]. Here the interest lies in estimating the absorbed radiation dose emanating due to an accident, i.e. in the case of situations where conventional synthetic dosimeters were not in place during the time of radiation exposure. The cause of accident can be due to nuclear weapons explosions, nuclear reactor accident or any event which results in unintended radiation release. Retrospective dosimetry, the conventional term used for this measurement, has been effectively undertaken for doses ranging from $\sim$ few mGy to few Gy using the $110°C$ glow peak of quartz. The high sensitivity of the $110°C$ pre-dose peak, using fired quartz grains, at relatively low doses makes it the only TL technique that is generally applicable for retrospective environmental dosimetry.

Retrospective dosimetry essentially involves reconstruction of the radiation dose received by the local population in the event of a nuclear accident. Different methods, based on the pre-dose mechanism, have been utilized effectively to estimate the dose leaked during all the major nuclear accidents. The measurements utilize natural minerals, like quartz, extracted from ceramic materials, like bricks, tiles, pottery, porcelain, cementitious building material etc., at the affected sites. The International Commission on Radiation has demonstrated the applicability of the fired clay bricks and the ceramic materials in buildings populated in regions affected by radioactive fallout to be reliable dosimeters to regenerate the dose profile of the accident radiation dose [72].

5.2 *Dating*

The memory effect of $110°C$ peak in the form of the pre-dose sensitization has been effectively utilized for dating the fired specimen [1,3,4,34,73]. As explained earlier, the technique based on this mechanism does not rely on the conventional build-up of the signal with time but the enhancement in the TL sensitization since the last firing episode. This method has been found quite powerful for samples which are a couple of thousand year old – archaeological time scales. The conventional TL methods do encounter limitations in this age bracket, mainly, due to poor TL signal. So, the age estimation of this era, a vital time period in the case of archaeological dating, is best suited for the pre-dose dating method. Various protocols, based on the pre-dose phenomenon, have been devised to enhance the reliability of the technique. Figure 9 illustrates applicability of the methods based on the pre-dose phenomena of, both TL and OSL signals in the estimation of the equivalent dose [74]. It demonstrates the dose recovery of the applied radiation dose, 4.46 Gy, using the additive pre-dose protocols of the two signals in the case of the pre-fired local geological sample, Thar. The recovered doses in the case of both the modes of the
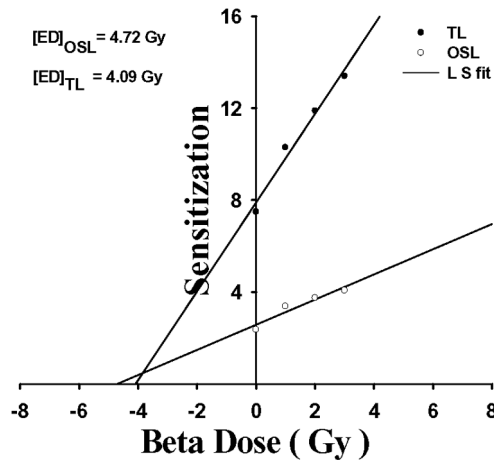
Figure 9. Dose recovery using TL and OSL additive pre-dose protocols in the case of pre-fired local geological quartz sample, Thar. A beta dose of 4.46 Gy, the dose to be recovered, was administered to the specimen. Additive doses of 1, 2 and 3 Gy were applied in the dose recovery protocol. The values of doses recovered using the TL and OSL pre-dose procedures were 4.08 and 4.72 Gy respectively. The correlation coefficients of the TL and OSL fits have been found to be quite good, 93.7 and 91.6% respectively [74].

luminescence, TL and OSL, were found to be close to the laboratory administered radiation dose, 4.09 and 4.72 respectively.

The pre-dose dating technique has also gained importance as a reliable tool in authenticity testing, especially for the kind of ware in which TL is affected by (i) spurious signal, (ii) anomalous fading and (iii) loss of TL signal which did happen due to some unwanted heating of the ware [75,76]. Various controversies related to the authenticity of the antiques, have been resolved by incorporating the advantages inherent in this technique which would not have been otherwise possible [1]. The pre-dose method assumes tremendous importance for objects older than 500 years, as the conventional method becomes highly unreliable in this range. This is the era which covers the Renaissance period, an era which has attracted scores of gifted forgers.

5.3 *Estimation of firing temperature*

Knowledge of thermal history during the firing event of the specimen has generated a lot of interest for two reasons: (i) to know whether the zeroing has been perfect and (ii) to select the protocols for TL and OSL dating measurements [48]. The former has a lot of bearing on the TL dating as perfect zeroing ensures its reliability. The sensitivity of the 110°C TL peak has been found to depend on the firing temperature, time of firing, rate of cooling and the heating environment. Methods based on the various aspects of the 110°C peak have been devised successfully to evaluate the firing temperature in a reliable way [77–80].
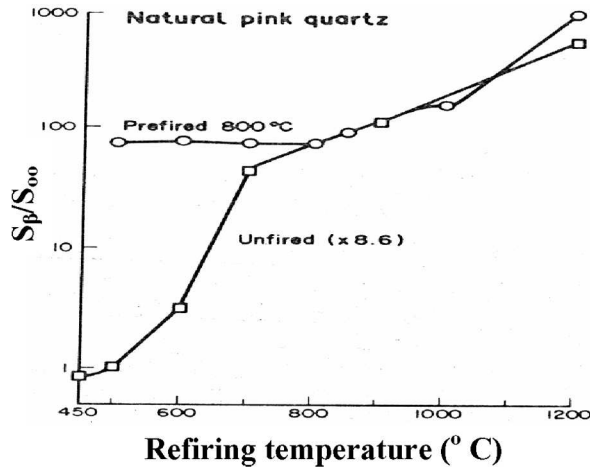
Figure 10. Sensitization curves of unfired and fired (800°C) quartz samples with refiring at various temperatures. The unfired specimen shows a monotonous growth with refiring while the fired one remains constant till the pre-fired temperature (800°C) and thereafter enhances with refiring [81].
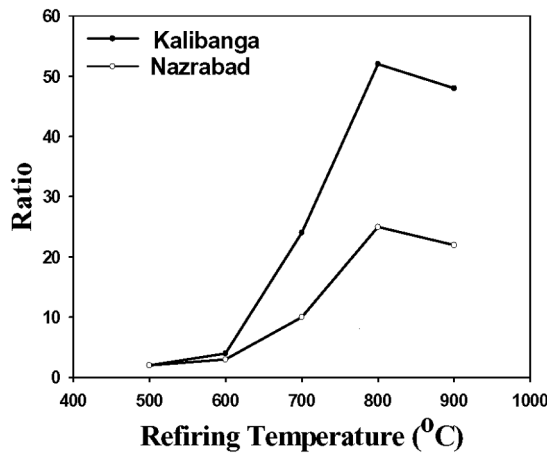

Figure 11. Sensitivity ratio, defined as the ratio of the pre-dose sensitized and un-sensitized 110°C TL signal, of the quartz samples from pottery samples, Kalibanga fabric 'c' and Nazrabad [32].

Pre-dose based technique has also been attempted for the identification of the firing temperature but with mixed results. In their studies, Sunta and David [81] could identify the firing temperature mark by observing the sensitization behaviour of the unfired and fired samples with different refiring temperatures (figure 10). Watson and Aitken [82] on the contrary did not observe any such pattern in the case of both fired and unfired samples. The validity of the technique was examined by Koul *et al* [32] using a wide spectral band. This band was chosen to minimize
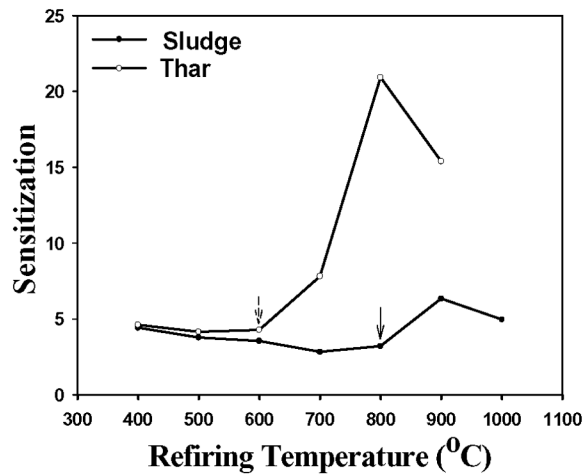
Figure 12. Measurement of the OSL sensitization of the Thar and Sludge samples after refiring at various high temperatures, 400–900°C in the case of Thar and 400–1000°C in the case of Sludge, in steps of 100°C. The pre-dose treatment consisted of a test dose of 0.4 Gy, pre-dose of 10 Gy and thermal activation temperature of 380°C. The arrows point out the firing temperatures experienced by the specimen prior to refiring, 600 and 800°C in the case of Thar and Sludge respectively [83].

the spectral changes, if any, during the firing process. The results of their studies also indicated that the technique might not be generally applicable (figure 11). The various aspects involved in this measurement were analysed to ascertain the applicability of the technique [84]. In this direction the role of alkali ions was postulated to limit the capacity of the 110°C peak of quartz to remember the firing temperature using pre-dose sensitization technique [85]. Recently, the applicability of the pre-dose OSL along with the pre-dose of the 110°C signals for the firing temperature estimation indicated that the overall pattern of the sensitization curves in the case of both TL and OSL emissions seem to carry the signatures of the phase transition rather than the firing temperature mark (figure 12) [83]. The variation in the sensitization might be attributed to the phase transition occurring in the temperature range of 800–900°C.

6. Correlation with OSL

Optically stimulated luminescence (OSL) is the luminescence emitted by irradiated insulator or semiconductor during exposure to light [86,87]. The phenomenon is analogous to TL with the stimulation being carried out by light instead of heat. On continuous exposure to the optical stimulation (420–550 nm) the OSL signal of quartz is observed to decrease continuously. The curves obtained during the optical stimulation are called OSL decay or shine down curves, similar to glow curves in TL measurements.

OSL has emerged as the most powerful analytic method for various applications. A number of studies have been undertaken by various workers to observe the relationship between the 110°C TL peak and OSL signal of quartz [22,36,37,88,89]. The two phenomena have been observed to respond in a similar fashion to (i) impact of thermal treatment [25,54,55], (ii) the pre-dose treatment [56] and (iii) the charge build-up during irradiation and the transfer of charges from R-centres to L-centres due to thermal activation in the pre-dose mechanism. All the features of the pre-dose phenomenon such as (i) growth curves (figure 13), (ii) thermal activation curves and (iii) impact of the UV have been reported to be very similar for both luminescence processes.

The correlation between the 110°C TL peak and OSL signal of quartz has been established to such a level that the former has been utilized, extensively, as a reference for OSL applications. The protocol employed in the case of OSL measurements involves pre-heating and to know what sort of bearing it will have on the OSL behaviour, the 110°C TL peak has been used as an effective handle [90]. So, this sort of correlation has rendered a lot of importance to the 110°C peak during the last few years. The luminescence centres responsible for the emission of the OSL signal at ∼370 nm have also been suggested to be the same ones that are used in the production of the 110°C TL peak [38,39]. However, this relationship between the two phenomena has been reported to be valid only for the fast component of the CW-OSL signal and not for the other components of this signal [91]. The behaviour of the two processes has been modelled extensively by Bailey [40].

Murray and Wintle [92] reported that the 110°C TL sensitivity was almost directly proportional to OSL sensitivity only if the annealing temperatures of the samples fall below 500°C. The annealing at high temperatures has been observed to favour the TL process. The dissimilarity in the ratio of the two sensitivities in the case of higher annealing temperatures was also reported by Chen *et al* [93] for sedimentary samples. In fact, Koul and Chougaonkar [83] found that with increase in the firing temperatures the TL/OSL ratio becomes larger in the case of both conventional and pre-dosed signals (table 1). To explain this variation in the behaviour of the 110°C TL and OSL with high annealing temperatures, Li [94] proposed a model which involves three electron traps, one type of luminescence centre and three non-radiative recombination centres (R-centres) – an extension of Zimmerman's model. It was postulated that the 110°C TL trap and OSL trap access different suites of R centres. Any deviations from this proportional relationship has been explained on the basis of preferential destruction of competing centres during the thermal treatment.

The concept of multiple R-centres, as explained earlier, was introduced by Bailey [40], and Adamiec [63] in order to explain various facets of pre-dose sensitization of the 110°C TL peak as mentioned above. The hypothetical correlation of these centres with these two modes of luminescence, proposed here, needs to be established firmly. Though variation of the pre-dosed (TL/OSL) ratio with different temperatures does support this argument to some extent (table 1), this hypothesis needs a better understanding. At the same time, it becomes worthwhile here to visualize whether the competing, deep centre, as described above, also has some role in this process. This centre, as explained in the previous sections, was conceived to explain various phenomena like sensitization and modification in the growth curve of the
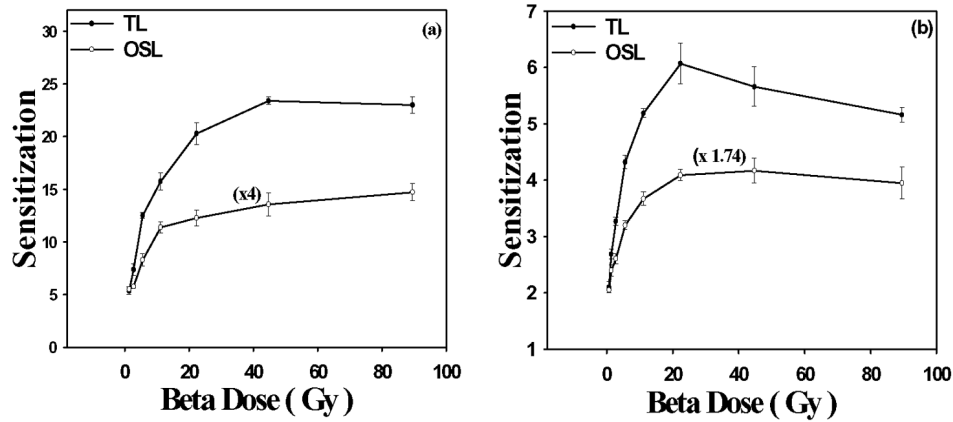
Figure 13. Growth curves of (**a**) Thar and (**b**) Sludge with the administered radiation dose (pre-dose) of 0.7, 1.4, 2.8, 5.6, 11.2, 22.4, 44.8 and 89.6 Gy in the case of Thar sample. The OSL growth curves are scaled up by a factor of 4. The treatments involved in the pre-dose measurements, apart from the pre-dose radiation dose, were a test dose of 0.4 Gy and thermal activation temperature of 380°C [56].

Table 1. Variation of TL and OSL signals with different firing temperatures. This is reflected by the ratio of the two emissions at these heating temperatures. The ratios are shown for both un-sensitized and sensitized signals for both Thar and Sludge samples [83].

Sample	Firing temperature (°C)	Un-sensitized sensitivity ratio (TL_0/OSL_0)	Sensitized sensitivity ratio (TL_β/OSL_β)
Thar	600	0.72	1.67
	900	15.74	6.98
Sludge	700	0.46	0.75
	800	3.6	4.48

110°C TL peak occurring due to thermal treatment. The bias of thermal treatment towards the TL mechanism indicates that the removal of these centres might selectively affect the TL process also. Studies to monitor the impact of deep traps on the behaviour of 110°C TL peak needs to be extended to the OSL mechanism also in order to get a feel of these deep traps *vis-à-vis* the OSL process. In short, the impact of different centres, R-centres as well as deep centres, on the kinetics involved in the two luminescence phenomena needs a detailed study.

7. Future challenges

Although a lot of work has been carried out to bring out the various facets of the 110°C TL glow peak of quartz, the phenomena governing the luminescence

process and the nature of trap and luminescence centres still seems to be speculative. Zimmerman's phenomenological model, no doubt, has been able to explain most of the experimental observations, but, it has not yet been verified independently. Although the properties of the centres associated with the 110°C peak have been the subject of many publications, the physical mechanisms operating during luminescence phenomenon are not clearly understood. The kinetics involved during pre-dose treatment resulting in the formation of pre-cursors to the centres involved in the luminescence process is, again, not on the firm footing. The contribution of the extrinsic and intrinsic centres in the entire luminescence mechanism seems to be far from resolved.

The impact of thermal treatment on the properties of this first glow peak of quartz must be formalized in order to segregate the influence of the competitor, deep centre, and phase transitions. The influence of thermal activation in the pre-dose process needs to be investigated beyond its conventional role of being just a charge transferring agent. The hypothesis of the existence of the multiple R-centres and the preferential bias of these centres towards TL and OSL processes needs a firm understanding. The correlation studies between the 110°C TL and OSL signals may unveil various features involved in their luminescence mechanisms which might not be possible by studying them in an independent mode. Over the years the number of the reservoir centres have risen from one to three and we never know whether it will freeze there only.

8. Summary

By summarizing the work carried out by various workers, it becomes apparent that though the pre-dose phenomenon of the 110°C glow peak has been applied efficiently in a variety of applications, the basic understanding of the various facets of this first glow peak of quartz has not been yet established firmly. These include the nature of defects; radiation- and thermal-induced defect centre transformations; and the kinetics involved in the luminescence process. Workers are busy in both experimental and simulation studies to get a better understanding of the various stages involved in the entire mechanism. The correlation with OSL has opened a new window which may be quite useful in this venture.

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