1.1 Introduction

The development of nano sized material and their probing through TL and OSL (thermoluminescence and optically stimulated luminescence) techniques for novel nano-phosphor discovery, has increased the number of promising useful phosphor substances in the dosimetry and dating research areas. Using ball milling technique, size of the material was optimized with respect to different parameters. Change in size of the material lead to development of additional centres into material which is responsible for changes in luminescence output. This view is based on the fact that research interest in recent years, in dating and dosimetry applications mainly focused around development of more sensitive phosphor. Since synthetic quartz is an eligible candidate as phosphor in dating and dosimetry applications in nano range of its particle size, the detailed study of nano synthetic quartz becomes very essential to develop it as a useful phosphor. This chapter includes a detail description about synthetic quartz, Thermoluminescence (TL), optically stimulated luminescence (OSL) and the plan of the present work.

1.2 Synthetic Quartz

Quartz can record the amount of ionising radiation, and it has exposed to as a latent signal within the crystal. Due to this ability, quartz is used as dosimeter. Description of the relationship between luminescence output and the defect is too complicated for natural quartz due to twins and many imperfections. Therefore, natural quartz has been replaced by the laboratory-grown synthetic quartz crystal for precise understanding of luminescence.

Laboratory grown synthetic quartz is pure, free from twins and impurities. The level of defects can be controlled during the production of synthetic quartz crystal by hydrothermal technique, due to which, it becomes very easy to understand the structure of the material along with luminescence properties. It is widely used in dating and dosimetry applications due to its high purity, crystalline quality and structure sensitive nature. Additionally, the irradiation and thermal history of the synthetic quartz are known- primarily. It is known not to have received any significant prior dose and thermal treatment[1]. Many scientists had reported their research about the use of synthetic quartz for the dating aspect[2-5]. TL and OSL characteristics of synthetic quartz are affected by various physical conditions such as annealing temperature, grain size, annealing hour, radiation dose etc.[6]

The particle size of quartz plays an important role in dating application. A. H. Ranjbar et al[7] have recorded the TL glow curves for different micron grain-sized clear fused quartz. He reported that, TL intensity increases with decreasing particle size up to 38µm, after that it decreases with decreasing in particle size of the material. The changes in TL pattern and luminescence emission were correlated with the sweeping of the centres during the grinding process.

In yet advanced studies, several workers[8,9] have recorded OSL decay curves at room temperature for single grains of 63-53µm. Before stimulation, the samples were annealed at different temperatures followed by beta doses. They have reported that for better OSL, either dose or annealing temperature should be at a critical level.

Bhushan and Kohler et al concluded that, nano sized particles exhibit a remarkable amount of variation in electronic, magnetic, optical and chemical properties of a molecule that are significantly different from those of the bulk[10,11]. The surface cross-section area per unit volume increases with decrease in grain size and active/inactive surface defects are responsible for changes in luminescence signals[12,13].

Siti Shafiqah et al. observed the effect of particle size on TL response of silica nanoparticles (80nm, 140nm, 550nm). They found that the 80nm sized silica particles produced the largest TL due to increased surface to volume ratio, providing more available thermoluminescence carriers[14]. Some researchers have attributed to confinement effects in nano-scale materials with the alteration in luminescence properties of luminescent micron and nano-structured ceramic. Phosphor powder is attracting considerable attention among different nano-materials due to their novel optical properties, which affect emission lifetime and luminescent efficiency[15]. The excellent result related to the luminescence efficiency of nano-ceramic material and silica nanoparticles have been reported. Therefore, in the present work, we have focused on TL and OSL of nano synthetic quartz for its use in dating and dosimetry applications which can be developed in future.

1.3 Luminescence

Luminescence is a process in which the material emits light as electrons return from an excited state to the electronic ground state. An electron emits light in the form of a photon which previously absorbed by an electron from some other energy source. Based on different excitation energy, there are various luminescence types:

a. Photoluminescence (excitation by optical or ultraviolet light)
b. Radioluminescence (excitation by nuclear radiation i.e. γ- rays, β- rays, X- rays etc.)
c. Chathodluminescence (excitation by electron beam)
d. Chemiluminescence (excitation by chemical energy)
e. Triboluminescence (excitation by mechanical energy)
f. Electroluminescence (excitation by electrical energy)
g. Bioluminescence (excitation by biochemical energy)
h. Sonoluminescence (excitation by sound waves)

Luminescence process takes place with two steps: one, absorption of energy and another, emission of light as a photon. Emission of light occurs within characteristic time τ_c after the absorption of radiation, and due to this parameter, the luminescence process can be classified into two type:

1. Fluorescence ($\tau_c < 10^{-8}$ sec) and
2. Phosphorescence ($\tau_c > 10^{-8}$ sec)

The value $\tau_c < 10^{-8}$sec indicates toward essentially spontaneous process of fluorescence. Fluorescence emission depicted during excitation itself and it stops with the removal of the excitation source. Whereas, phosphorescence characterized by a delay between the radiation absorption and the time ‘t’$_{max}$ to reach full intensity. It means that, phosphorescence is continued for some duration after the excitation has been taken out. Phosphorescence divided into two subparts, namely, short-period ($\tau_c<10^{-4}$sec) and long-period ($\tau_c>10^{-4}$sec) phosphorescence. The time spends by an electron in electron trap is directly correspond to delay in phosphorescence. Mean time expended in the trap at temperature T is given as:

$$\tau = s^{-1} \exp\left(-E/kT\right) \qquad \text{Eq. 1.1}$$

Where s is a constant and E is the energy difference between excited state and trap level, k is Boltzmann's constant. Therefore, the mean lifetime is exponential dependent upon temperature[16]. Mean lifetime will be greater for deep trap, i.e. mean lifetime can be reduced by increasing the temperature. Thus, luminescence can be observed from deep trap and luminescence emission which is obtained by thermal stimulation is called Thermally Stimulated Luminescence or Thermo luminescence (TL). Alternatively, if stimulation is caused by optical energy, then luminescence emission is called Optically Stimulated Luminescence (OSL). From the last many decades, such type of dose-dependent luminescence have been widely used for either dating of the archaeological specimen and geological sediments or radiation dosimetry, i.e. determination of the integrated radiation dose to humans[17].

1.4 Thermally stimulated luminescence (TSL)

Thermoluminescence (TL) has been first used by Daniels et al. to measure nuclear radiation doses since 1950s. TL technique was also used for archaeological dating in the early 1960s (e.g. Aitken et al, 1964; Aitken et al, 1968; Mejdahl, 1969) and geological dating in the beginning of the 1980s (e.g. Wintle and Huntley, 1980)[17].

Thermoluminescence (TL) is the light emitted by heating the material at a constant rate up to a certain temperature which has previously exposed to ionizing radiation. Thermo luminescent material may be exposed to all types of radiations such as α, β, γ-rays, X-rays and light rays. The essential condition is that, material should be semiconductor or insulator to produce Thermoluminescence. TL is recorded by heating material at a constant rate to some temperature and display of TL signal is to plot luminescence intensity as a function of temperature, known as a TL-glow curve (Fig. 1.1).

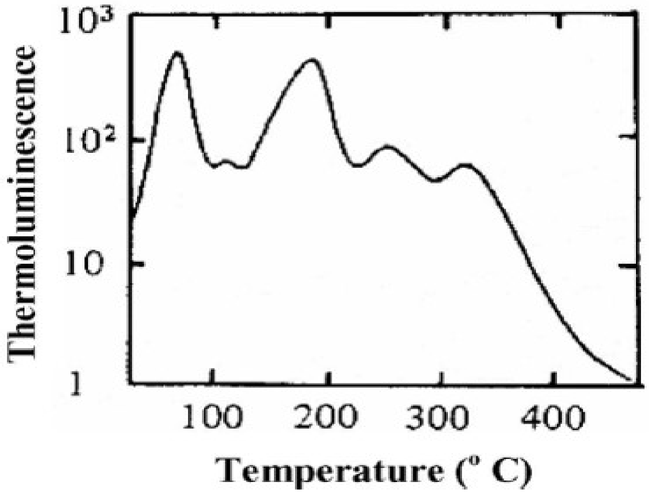
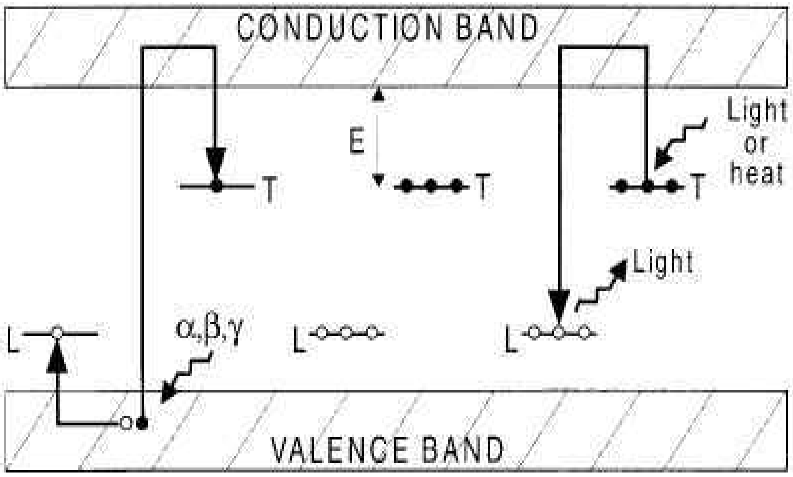


Fig. 1.1 TL glow curve of the natural pink quartz[18].

Several peaks observed at different temperature in TL glow curve, which is related to electron traps that are present in the material. These traps are due to the presence of defects in the lattice structure. The absence of a negative ion creates a typical point defect, which provides a negative ion vacancy and acts as an electron trap. Thermal vibrations of the lattice will finally knock out a trapped electron from electron trap. These thermal vibrations become stronger by raising the temperature of crystal lattice and the probability of ejection increases quickly, so within a narrow temperature range, trapped electrons are released rapidly. From these, some electrons give rise to radiative recombination with trapped holes and emit energy in the form of light (TL). Fig. 1.2 indicates different stages of TL process. Where T is Electron Trap, L is Luminescence Center, open and closed circles are hole and electron respectively. At the first stage, ionization takes place due to the exposure of nuclear radiation with the trapping of electrons and holes respectively at T and L defects. The second stage is the storage of radiation energy, during that time, if the leakage of energy is negligible then much longer storage time of the sample is required for the lifetime of an electron in the trap. This lifetime is dependent on trap depth E below the conduction band. The third stage is heating the sample or signing with light energy; electrons will be removed from the electron traps (T) and some of these will reach at luminescence centres (L); resultant light emitted as a consequence of recombination process performed at these centers[19].



(a) Ionization **(b) Storage** **(c) Emission**

Fig. 1.2 Energy diagram of TL and OSL process. Different stages are involved in TL/ OSL process: (a) electron and hole are created, (b) charge storage at trap and (c) stimulation and light emission[19].

Luminescence phenomenon has been described through the energy band model because the energy band model is useful to understand the process of transport of an electronic charge through the lattice. Above described thermoluminescence phenomenon is known as a simple model. There are other thermoluminescence models such as additions to a simple model, an alternative model and more complex models etc.

Emission of the light by the phosphor during thermoluminescence process is proportional to the amount of radiation dose absorbed by the phosphor, which has been previously exposed by the source of radiation. Therefore, this technique can be used to measure absorbed dose by the material, and it is a very highly sensitive technique to detect the presence of defect centres in the material which are responsible for the TL output signals.

Many TL materials suffered due to thermal quenching problem wherein the luminescence efficiency decreases with a rise in temperature. Thus, results in alteration of the crystal occurred. On the other hand, OSL generally measured at near to room temperature. So, the problem of thermal quenching is avoided in OSL and sensitivity of OSL procedures is also higher than TL procedures. Therefore, the OSL technique is better than compared to TL technique[20].

1.5 Optically stimulated luminescence (OSL)

The OSL technique was first implemented by Huntley et al. (1985). He used the green light from an argon laser (514 nm) to stimulate luminescence from quartz for the optical dating of sediments[17]. Optically stimulated luminescence (OSL) is observed as a result of the recombination of charges, which is optically released from electron traps within the crystal. Excitation (exposing by ionization radiation) put electrons and holes separately trapped at defect centres in the crystal. Then during OSL process, light stimulates these electrons and holes from these traps. Consequently, resultant electron/hole recombination and excitation of luminescence centres in the crystal is obtained. [Fig.1.2] The effect of irradiation of the material is the electron population in the traps, so the OSL intensity is correlated to the absorbed radiation dose. These electron/hole traps may or may not be the same as those traps which are associated with the TL peaks. OSL signal observed to decrease to a low level as the trapped charge is dwindling (decay curve) during exposure to the stimulation light. There are three types of optical stimulation; Continuous Wave OSL, Linear modulated OSL, Pulse OSL.

The OSL technique used in this research is not to be confused with the PL that stimulated with similar materials. When light is used primarily for the aim of determining the defect's structure by exciting the electron with a photon from the defect's ground to defect's excited state, and then resultant luminescence is called PL. However, OSL results in an irradiated material when stimulated with light[21].

The general description of OSL, the intensity of the luminescence emitted, is related to the rate at which the system returns to the equilibrium. The rate at which equilibrium restored is a function of the concentration of trapped charge. Generally, one observe, the intensity of light as a function of time, resulting in a characteristic luminescence –versus- time curve. Consequently, the integral of the luminescence-versus-time curve is related to the concentration of trapped charge, which is proportional to the initial dose of the absorbed radiation[22]. The OSL signals observed to decrease to a low-level during exposure to the stimulation light as the trapped charge depleted. The curve is known as the OSL decay curve.

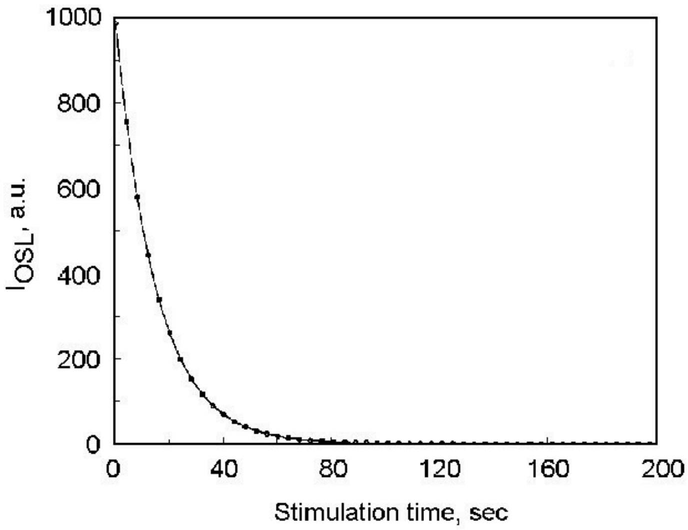


Fig. 1.3 OSL decay curve obtained from sedimentary quartz sample[23].

According to the aim of the investigation, optical stimulation can be performed in three ways. First, continuous-wave OSL (CW-OSL) method, in which the light intensity of stimulation is kept constant and OSL signal continuously monitored throughout the stimulation period. Second, Linear-modulation OSL (LM-OSL) method in which the stimulation intensity ramped linearly while the OSL is measured, and third, Pulse OSL (POSL) method in which the source of stimulation is pulsed and the OSL observed only between pulses[22]. In the present research work, CW-OSL method is used because of the constant stimulation light intensity. General representation of traps having various photoionization cross-section, which is the probability of interaction of trapped electrons with a photon obtained from this process. Where discrimination of the light of stimulation and light emitted is required. The phenomenon accomplished by using the combination of suitable optical stimulation and detection filters. So, as it happens, the OSL traps with certain energies can be examined, and emission observed in this stimulation mode in a specific wavelength. The shape of the OSL signal obtained in the form of luminescence decay curve, following an exponential like function is shown in the Fig. 1.3.

OSL technique has number of advantages over TL technique. In OSL, Optical readout method means no heating required to the samples. Thermal quenching problem in TL is solved by OSL technique because readout in OSL performed at a lower temperature. OSL responded only the components of the trapped electron population which are most sensitive to light. These components are most likely to be voided (or "reset") during transport, before deposition and burial that is why this is important in geological dating. One of the major advantages of OSL over TL is that, OSL measured at or close to room temperature. So, alteration of the crystal minimized. Therefore, the OSL method has higher sensitivity compared to TL method. OSL also recorded at elevated temperature which permits for selective analyses of traps at different light sensitivities[20].

1.6 Models of OSL

In general, the shape of an OSL decay curve cannot be investigated using simple descriptions. The decay is often non-exponential, typically displaying a long tail at long illumination times. Under certain conditions, and for some specimens, even after the illumination is applied, the OSL can display an initial slow increase, followed by the more normal decrease over longer periods. A long tail in OSL decay curve is produced either by the effect of shallow traps or contribution from traps. Where, the impact of shallow traps that localized charge released during illumination and slowly rerelease them at a rate of determined by trap depth and sample temperature, and contribution from traps, that are emptying slowly at the excitation wavelength used in the experiment. Hence, the shape of the decay curve depends on the specimen, absorbed dose, illumination intensity and temperature.

The OSL process can be mathematically described by the sequence of intractable non-linear, coupled rate equations. Therefore, some models that were previously introduced to understand a solid structure are used to apply them to experimental results to understand the sample's OSL properties. Among these models, the simplest one is the one-trap/one –centre model[24].

1.6.1 Simplest Model: one trap/one center

To reach recombination site, most OSL models presume transportation of the optically excited charge through the delocalized bands. Fig. 1.4 (a), showing the simplest model that includes one type of electron trap and one type of hole trap. Light stimulates to the trapped electron into conduction band with rate f, they recombine with the trapped hole to produced OSL intensity I_{OSL}, or they are re-trapped. Before describing this phenomenon mathematically, first, total charge neutrality for this system should be written as:

$$n_c + n = m_v + m \qquad \text{Eq. 1.2}$$

Where n_c and n are the concentrations of electrons in the conduction band and traps, respectively. m_v and m are the concentrations of holes in the valence band and hole traps, respectively.

Transitions to the valance band do not occur during optical stimulation of the electrons from the traps. Therefore, the charge neutrality condition turn into $n_c + n = m$. then the rate of change of the various concentrations can be written as:

$$\frac{dn_c}{dt} = -\frac{dn}{dt} + \frac{dm}{dt} \qquad \text{Eq. 1.3}$$

The term on right side may be written clearly as:

$$\frac{dn}{dt} = -nf + n_c A(N - n)) \qquad \text{Eq. 1.4}$$

And

$$\frac{dm}{dt} = -n_c A_m m = -\frac{n_c}{\tau} \qquad \text{Eq. 1.5}$$

Here, f is a positive function of the incident photon flux ϕ and the photoionization cross –section σ for the monochromatic light.

$$f = \sigma\varphi \qquad \text{Eq. 1.6}$$

Where equation (1.4) and (1.5) include A-the re-trapping probability, A_m-the recombination probability, N-the total available concentration of electron traps, and $\tau = 1/A_m m$ is free electron recombination life time. If Quasi- equilibrium ($dn_c/dt << dn/dt$, dm/dt and $n_c << n, m$) and negligible re-trapping ($n_c A(N-n) << nf$, $n_c A_m m$) are assumed. Then

$$I_{OSL} = -\frac{dm}{dt} = -\frac{dn}{dt} = nf \qquad \text{Eq. 1.7}$$

The solution of which is

$$I_{OSL} = n_0 f \exp(-tf) = I_0 \exp(-t/\tau_d) \qquad \text{Eq. 1.8}$$

Here, n_0 is the concentration of trapped electrons at time t=0, I_0 is the luminescence intensity at t=0, and $\tau_d = 1/f$ is the decay constant. From this equation, it is observed that OSL decay curve has a simple exponential curve and OSL intensity becomes zero in the end when all the traps are emptied.

1.6.2 Competing, deep trap

Experimentally, OSL decay curve does not confirm that it is a simple exponential form. The reason behind this is that these curves may involve significant re-trapping process or different types of traps that have different photo-ionization cross-sections. Smith and Rhodes interpreted their data by fitting to the observed non-exponential OSL decay curve. They stated that, OSL decay curve is the sum of three exponential decay curves with varying values for the decay constant- named as "fast (F)", "Medium (M)" and "slow (S)" components[25]. So, Chen and Mckeever resolve the case of re-trapping[26]. If there are two optically active traps (n_1 and n_2 are concentration and f_1 and f_2 are stimulation rates) as shown in Fig 1.4 (b), then

$$\frac{dm}{dt} = -\frac{dn_1}{dt} - \frac{dn_2}{dt} \qquad \text{Eq. 1.9}$$

Along with charge neutrality condition of $n_1 + n_2 = m$

We have,

$$n_1 = n_{10} f_1 \exp(-tf_1) \qquad \text{Eq. 1.10}$$

And

$$n_2 = n_{20} f_2 \exp(-tf_2) \qquad \text{Eq. 1.11}$$

Thus,

$$I_{OSL} = n_{10} f_1 \exp(-tf_1) + n_{20} f_2 \exp(-tf_2)$$

$$I_{OSL} = I_{10} \exp(-t/\tau_1) + I_{20} \exp(-t/\tau_2) \qquad \text{Eq. 1.12}$$

This equation is sum of two exponentials. If second trap is optically inactive and act as deep one then the OSL intensity is described as:

$$I_{OSL} = n_{10} f \exp(-tf) - dn_2/dt \qquad \text{Eq. 1.13}$$

Where;

$$dn_2/dt = n_c(N_2 - n_2)A_2 \qquad \text{Eq. 1.14}$$

According to the standard definition and additional assumption that, $N_2 >> n_2$ then $n_c N_2 A_2 \sim$ constant C.

Hence,

$$I_{OSL} = n_{10} f \exp(-tf) - C \qquad \text{Eq. 1.15}$$

Where, for the deep trap N_2, n_2 and A_2 are the concentration of available traps, concentration of filled traps and trapping probability, respectively. From equation, OSL intensity is reduced due to re-trapping into deep trap[21].

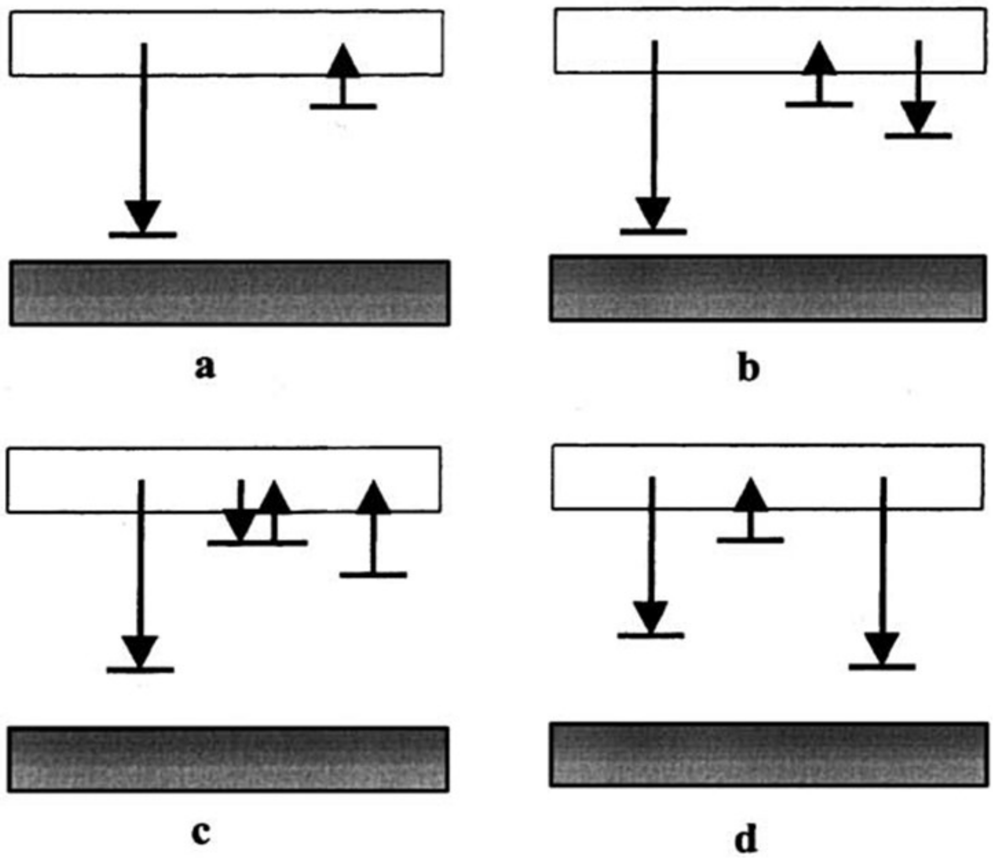


Fig. 1.4 Different Models for OSL (a) Simple model: one trap and one recombination center, (b) Model containing competing deep trap, (c) Model involving shallow competing trap, (d) Model having competing recombination center[27].

1.6.3 Competing shallow trap

Shallow traps are depicted in Fig. 1.4 (c). If shallow traps are considered as competing trap which are thermally metastable at the temperature of the OSL measurement then Equation 1.13 becomes,

$dn_2/dt = n_c(N_2 - n_2)A_2 - n_2 p$ Eq. 1.16

Where, p is the rate of thermal excitation out of the trap. Now

$I_{OSL} = n_{10} f \exp(-tf) + n_c p - n_c(N_2 - n_2)A_2$ Eq. 1.17

The last two terms in equation (1.15) combine to develop a long-lived, temperature dependent tail to the OSL decay. This component's form is an initial rise, followed by decrease at longer times. The overall OSL decay curve may exhibit an initial rise followed by a decrease, depending on the relative size of this component compared to the first term. The relative size of the two components also depends on the rate of excitation p so that the temperature – dependent term may be significant at low p values[24].

1.6.4 Competing recombination center

For the case of two recombination centers shown in Fig. 1.4 (d), in which one m_1 is radiative and other m_2 is non-radiative. Then $n= m_1+ m_2$,

$n = n_0 \exp(-tf)$ and, $I_{OSL} = n_0 f \exp(-tf) - dm_2/dt$ Eq. 1.18

As in case of deep trap, the OSL intensity is decreased by presence of a non-radiative recombination center. Quasi- equilibrium ($dn_c/dt \sim 0$) leads to:

$m_1 = m_{10} \exp(-tn_c A_{m1})$ Eq. 1.19

and,

$m_2 = m_{20} \exp(-tn_c A_{m2})$ Eq. 1.20

Where, A_{m1} and A_{m2} are the recombination probabilities at the two centers, respectively. The relative size of the recombination centers is time- dependent, thus:

$\frac{m_1}{m_2} \approx \frac{m_{01}}{m_{02}} \exp(-tn_c\{A_{m1} - A_{m2}\})$ Eq. 1.21

In the situation that $A_{m1} \sim A_{m2}$, the ratio remains approximately constant. So, in this case OSL decay curve remain approximately exponential, then

$I_{OSL} = \frac{1}{K} n_0 p exp(-tf)$ Eq. 1.22

Where, K is constant and $K=(m_1+m_2)/m_1$. If we compare equation (1.20) with equation (1.7), it is seen that former case gives weaker OSL signal by factor 1/K[22,24].

The Models described above showed a very special case only. Since real materials can have all types of the electron traps together with recombination centres. Therefore, the OSL decay curve achieved for these materials is much more complex. On the other hand, this difficulty can be overcome by understanding experimental results in light of the necessary information achieved from these models[21].

1.7 TL of synthetic quartz and its Literature survey

In 1950s, Danieal et al. published their research about extensive use of thermoluminescence to evaluate nuclear radiation dose[28]. Then TL technique was applied for archaeological dating in the early 1960s[29-31] and for geological dating in the beginning of the 1980s[32]. Since the early 1970s, quartz has been used extensively in TL dating[33]. Researchers identified that the natural and synthetic quartz exhibited number of TL glow peaks when irradiated sample was heated at constant heating rate above room temperature to 500°C which was centred around 95-110°C, 150-180°C, 200-230°C, 305-325°C, and 375°C (depending on the heating rate)[34-37]. Then some authors had explained that TL emission of TL glow peaks of natural and synthetic quartz was centred around 370, 470 and 620nm[38-41]. For dating purpose, thermal treatment is a necessary parameter. So, in 1997 Wintle et al. explained its effect on TL properties of the crystal[2]. Some authors had explained the influence of different pre-treatment on TL of natural quartz and they reported that sensitivity of quartz was increased with thermal treatment[42-45].

In 1971, Zimmerman was suggested a phenomenological model. The Model explained pre-dose sensitization that was based on the transfer of charge from one recombination centre to another. Pre-dose sensitisation treatment involved combined effect of radiation and heat treatment[42]. Chen et al. supported to Zimmerman model and reported that annealing of synthetic quartz remove the competitor which resulted in the decrease of super linearity which was related with the increase in sensitization[43]. Scientists had observed the effect of heating and irradiation on TL glow curves for a number of synthetic forms of quartz[3]. Studies revealed the effect of irradiation temperature and annealing temperature on the TL properties of synthetic quartz and suggested that the sensitization followed by radiation could be due to removing of competitor traps[46]. Reports had been published about the study of superlinearity of synthetic quartz for slowly pre-dose samples and for annealed samples. They found the same effect of decreased superlinearity with increased sensitivity under heavy pre-dose irradiation of the samples[47,48]. Benny et al. supported the above theory, and they showed that the decay of E_1' centre appeared in thermally annealed quartz samples and E_1'-centers were observed after UV bleach which supported the role of competing traps and the involvement of E_1' centres in pre-dos sensitization[49].

Dependence of sensitivity on the grain size of some materials had also been suggested by Horowitz[50]. In 1990, a research article revealed the dependence of the TL outcomes on the grain size of synthetic quartz and explained that the sensitivity of the samples decreased with smaller grain size and dose dependence TL curves changed with the grain size[4]. After almost two decades, a research reported the effect of particle size in the TL response of natural quartz sensitized by high dose gamma radiation and heat treatment. They explained the results in relation with the specific surface area of quartz particles and the involvement of intensity of ESR signal of the E'_1 center in the sensitization process[5]. A group of scientist had worked on the crushing effect on TL and OSL signals in quartz to examine the practicability of using OSL and TL for dating of faulted rocks and concluded that 100°C TL sensitivity was decreased after crushing the sample and OSL signal intensities were variably increased after crushing especially for small grain size fractions[51].

Here we discuss about the TL peaks:

110°C TL peak

110°C TL peak is also known as traditional pre-dose peak and it is observed around 95-120°C in glow curve region. The peak has maximum emission centred on 360-380nm, 420nm and 450-470nm. Based on ESR, IR and luminescence measurement, it is observed that the trap responsible for this peak are the $(GeO_4)^-$ electron traps and the centres $(AlO_4)°$ and $(H_3O_4)°$ act as recombination centres. Correlation between 110°C peak and OSL signal of quartz is well established and used as a reference for OSL applications. In the form of pre-dose sensitization, this TL peak is used for dating application related to fire specimen[18].

210°C TL peak

Researcher observed glow TL peaks in synthetic quartz, and they concluded that 210°C peak is stable at higher annealed temperature and centred on 410nm emission wavelength. They also concluded that this TL peak is suitable for dosimetry and dating applications[8,9]. Researcher studied the radiation induced sensitization in quartz and they found Ge-center, E_1' center, and both are correlated with 210°C peak and involved in the sensitization process of 210°C peaks in quartz[52].

325°C TL peak and 375°C TL peak

325°C TL peak in quartz is known as rapidly bleachable peak having its emission wavelength at 380nm. While 375°C TL peak in quartz is known as slowly bleachable peak having its emission wavelength at 480nm. So 375°C TL peak is extensively used for dating applications for quartz [8,9].

Other TL peaks

Several other TL peaks at 150-180°C and 280°C are also observed in the glow curve, which is rapidly bleached by exposure to light. Franklin et al., studied emission wavelength of Australian quartz and reported that 150-180°C rapidly bleachable peak is centred at 392nm emission wavelength[8,9].

1.8 OSL of synthetic quartz and its Literature survey

With further development in research, scientists faced some limitations with the TL technique during experimental work. So, use of OSL technique has been introduced in place of TL technique for applications for dosimetry and dating. Huntley et al. worked on this issue and revealed an aspect that a good luminescence signal could be found from quartz by using optical stimulation rather than thermal stimulation. They stimulated quartz by using the 514.5nm single green line from an argon-ion laser to use this method in optical dating of sediments[53]. This method had also been developed more recently for archaeological dating and dosimetry.

The advantages of OSL over TL are rather understandable in the applications. Scientists had explained that the OSL signal from quartz could be stimulated by using a broadband light source produce a blue-green light spectrum (420-550nm)[54,55]. They further studied that the continuous wave OSL (CW-OSL) method was particularly more precise in geological dating and accident dosimetry[56]. S W S Mckeever et al. had studied the defect pattern using OSL decay under the physical conditions such as temperature, pressure, ionizing radiation and mechanical actions such as grinding, crushing, etc. and established the definite correlation between defects and OSL sensitivity[57]. He reported that the dose-response of OSL decay curve was an essential factor in any dating procedure and these outcomes can be used to estimate the equivalent dose in dating[58].

Some researcher studied the effect of ionising radiation under the identical physical condition on OSL decay curve of synthetic quartz at room temperature. It explained the fact that OSL decay showed slow exponential decay under below critical dose and above critical dose, OSL decay pattern was changed. They also explained that the change with dose was observed in annealed sample and E_1' center was responsible for slow decay which was observed in ESR spectra[59]. The group also reported the role of annealing temperature at a given radiation dose and the duration of annealing treatment on OSL sensitivity and shape of decay curve of synthetic quartz at room temperature. They found that phase change in synthetic quartz with increased annealing temperature was responsible for the change in OSL sensitivity[6]. Whereas other scientists had concluded that 380 nm emission luminescence centre and the family of TL traps were directly correlated to the traps giving rise to the OSL signal[60,61].

In 1997, some reports were published and explained that the traps associated with the 110°C TL peak are optically sensitive[62,63]. They suggested that OSL decay curve was observed with the sample held at 125°C, which keep empty the 110°C TL peak traps during optical stimulation[62]. It was also studied and concluded that this elevated temperature stimulation contributes a faster response, a smaller long time-constant component within the OSL decay curve and progress in measurement sensitivity[64]. Bailey et al. studied the three exponential components by obtaining quartz OSL at elevated temperatures and identified that the fast and medium components were related with the 325°C TL peak trap whereas the slow component remained stable until at least 650°C[63].

It was reported that quartz crystal bleached considerably more rapidly than that of feldspars because coarse grain usually contributes to greater scatter of data than for fine-grain methods[65]. To overcome this problem of large scatter, Rees-jones used fine grain of quartz for optical dating and concluded that the fine-grain quartz had great potential for use in optical dating[66]. Many researchers had also worked with fine grain size of quartz for dating application by using TL and OSL technique[65-67].

Several components of discrete type traps were resolved from the bulk OSL signal which emitted from sedimentary quartz, widely known as Ultra-fast, fast, medium and slow component. Ultra-fast component was found in initial part of OSL decay curve[68]. Components can be resolved and identified by mathematically fitting of CW-OSL curves. The fast component is most suitable for the dating purpose because it is highly light sensitive and thermally stable. Slow component is relatively slowly depleting portion of OSL decay of the quartz. It is distinct from the main 'rapidly bleached' portion of OSL decay signal (that dominated by fast and medium components) which is used in optical dating, Slow component has high thermal stability and high dose saturation characteristics which suggest much potential for long-range dating[69]. Different components of quartz have different characteristics with respect to photoionization cross-sections, dose saturation level, thermal stability and sensitivity. Photoionization cross-sections of a trap is an important parameter. This parameter revealed the optical sensitivity of a trap at a given wavelength. It was also shown that, which wavelength is optimum for stimulation during OSL measurement[27,70].

1.9 Aim, Objective and Approach

For the dating purpose, the grain size of the sample is most significant and crucial. The grain size of the sample depends upon grinding process of the material. Researchers[10,11] observed and explained the significant and noticeable variation in electronic, magnetic, optical and chemical properties of a molecule with the change in grain size from bulk to nano-metric level. Literature also revealed that the new active/inactive TL and OSL sites were observed due to increased surface area after reduction in grain size of sample by grinding process[12,13].

To understand the TL/OSL properties of nano particle sized synthetic quartz material, the present work, is aimed to TL and OSL studies of nano particle sized synthetic quartz specimens followed by different physical treatments. These studies further explore possibility to suggest its novel application as a radiation dosimeter. The interpretations of the outcomes of the TL/OSL results have been correlated and hence confirmed with different characterizations of the nano particles such as Particle size analysis, EDS, SEM, TEM, XRD, FTIR etc. Response of the physical treatments to nano quartz specimens are corroborated with the changes in luminescence properties. The outcomes are also resolved by the TL measurements, components of OSL decay curves and Electron Spin Resonance (ESR) study.

Prior to OSL and TL measurements, as the detailed study of physical structure/characterization of the nano sized quartz specimen, the following characterizations have been adopted for the conformation of the surface morphology, size of nano scale and composition of the material.

Nano-sized synthetic quartz sample was prepared by ball milling process so there was possibility of the presence of metallic contamination or process impurities in the material. Therefore, the purity of nano sized samples was checked by EDX technique and was found pure. The particle size analysis showed average grain size of prepared sample was 87 nm. The SEM analysis further confirmed that the particle size was in nano scale, but shapes of the particles were irregular and agglomerated. The TEM image also described that the particles of the sample are in nano range (below 100nm). The crystalline size of 39.41nm was confirmed by XRD analysis of prepared sample. The presence of hydroxyl group has confirmed by the FTIR analysis in the prepared nano sized synthetic quartz samples.

Further, to study response of nano grains towards the thermal treatments for luminescence output, the following experiments were performed.

Optical Absorption Study for un-annealed and annealed samples followed by beta doses:

Optical absorption spectra were recorded to understand the absorption of light capacity by attribute color centers, which may be available in nano synthetic quartz under the influence of physical conditions under study. Un-annealed samples followed by 2.52Gy and 5.04Gy beta doses have exhibited optical absorption intensity around 0.14 to 1.664 a. u for broad range of peaks from 200-258nm. The positions of these peaks remain identical but notable absorption by 2 to 2.5a.u was observed under the influence of pre-heat treatments such as 400^{o}C, 600^{o}C and 1000^{o}C annealed sample followed by 25.2Gy dose as compared to un-annealed samples.

PL Study for un-annealed sample followed by beta dose:

PL study has revealed the suitable wavelength (470nm) as a stimulation source in OSL process. The nano sized quartz sample exhibits broad emission wavelengths from 371nm to 493nm under 254nm wavelength of excitation.

TL Study from 25-398^{o}C for un-annealed and annealed sample at different temperature followed by beta doses:

To understand the contribution of the thermally sensitive traps and changes in their position under different thermal conditions, TL study was undertaken for un-annealed and annealed (at 400°C, 600°C, and 1000°C) nano samples followed by different beta doses. Un-annealed specimens followed by beta exposures of 48.03Gy, 81.43Gy and 120Gy exhibit usual TL glow peak at 110^{o}C along with the development of TL peak at 300^{o}C. However, the 300^{o}C TL peak disappears while exhibiting new TL peaks at 165^{o}C and 220^{o}C along with 110^{o}C TL peak under the influence of higher exposures beyond 120Gy.

The position of 110^{o}C TL peak remains invariant in 400^{o}C, 600^{o}C and 1000^{o}C annealed sample of 1hour duration followed by identical beta exposures. However, for 400^{o}C and 600^{o}C annealed samples do not show 165^{o}C TL peak and shows large variation in 220^{o}C TL peak position up to 293^{o}C with TL counts. The reappearance of 165^{o}C TL peak and thermal stability of 220^{o}C TL peak with growth in TL counts are observed in 1000^{o}C annealed sample. The TL sensitivity was found to be enhanced with thermal treatment compared to un-annealed specimen. The strength of 110^{o}C TL peak decreases with rise in annealing temperature to the samples.

OSL Study at 25^{o}C for un-annealed and annealed sample at different temperature followed by beta doses:

To observe the contribution of the optically sensitive traps and shape of the OSL decay curve under different physical conditions, a systematic study was carried out for un-annealed and annealed (at 400°C, 600°C, and 1000°C) nano samples followed by different beta doses. The un-annealed samples were exposed to 15.76Gy, 48.03Gy, 81.43Gy, 120.83Gy, and 160.23Gy and 199.63Gy beta dose followed by optical stimulation by 470nm at 25^{o}C for 100seconds. It is observed that very rapid OSL decay within 0.4 seconds of stimulation and usual OSL decay is seen for 0.4 seconds to 100 seconds in each exposed sample. Nearby 93% of OSL counts from its maximum values are dropped as a rapid decay and nearby 7% of OSL counts are dropped as a usual decay under exposed samples up to 120.83Gy. Beyond 120.83Gy beta doses, the pattern of decay curves is sustained over stimulation times but percentage of “rapid decay” is decreased to 46% and percentage of “usual decay” has increased by 54% of OSL counts.

However, the rapid decay is limited to 87% in lower annealed samples (400^{o}C and 600^{o}C) and further it has reduced to 56% in higher annealed sample for all exposures compared to un-annealed sample. The OSL sensitivity under influence of beta doses is weaker in 1000^{o}C annealed sample than lower annealed and un-annealed materials.

TL Study from 25-398^{o}C after OSL decay at 25^{o}C for un-annealed and annealed sample at different temperature followed by beta doses:

It is necessary to observe that thermally sensitive traps are still contribute in output signals or not, after OSL readout, TL glow curves were recorded. The correlation between OSL and TL signals were also carried out to reveal many undergoing physical processes. The un-annealed sample shows three distinct TL glow peaks at 110^{o}C, 165^{o}C and 220^{o}C after the optical stimulation near room temperature. The position of 220^{o}C TL peak is varied in lower annealed (400^{o}C and 600^{o}C) samples and it is re-established in 1000^{o}C annealed sample followed for identical beta doses. The noticeable thermal stability and dose dependent growth in 220^{o}C TL peak is observed in both samples.

OSL Study at 160^{o}C for un-annealed and annealed sample at different temperature followed by beta doses:

Un-annealed and annealed samples were irradiated by identical beta doses followed by optical stimulation at 160^{o}C for 100second. The un-annealed specimen shows nearby 96% of rapid decay within 0.4seconds of stimulation and around 4% of usual decay under influence of beta doses up to 120.83Gy. Beyond 120.23Gy doses, the percentages of rapid decay are limited to 40%. The lower annealed samples exhibit nearby 89-95% of rapid decay and higher annealed sample exhibits nearby 40% of rapid decay. The OSL dose response in 1000^{o}C annealed sample is weaker than lower annealed samples but better than un-annealed samples.

TL Study from 25-398°C after OSL at 160°C for un-annealed and annealed sample at different temperature followed by beta doses:

In order to study 220°C TL peak under these physical conditions only, the optical stimulations at 160°C for 100seconds by 470nm light is given to erase the contribution of lower temperature TL peaks. The variation in 220°C TL glow peak is observed over identical exposures in un-annealed material but the stability of this peak is observed along with the growth of new TL peaks around 325°C in 1000°C annealed sample.

ESR Study for un-annealed and annealed samples followed by beta doses-

ESR study is performed to observe the contribution of defect centers which are taking part in TL and OSL outputs of nano synthetic quartz samples. ESR is recorded for un-annealed and annealed samples followed by beta doses. Either for un-annealed or lower annealed samples show significant involvement of low temperature TL traps which are attributed to the available E_1' centers. The losses of luminescence counts are discernible to diminishing of E_1' centers and growth of new centers, which can be confirmed with the development of higher temperature TL glow peaks in 1000°C annealed material.

Based on the TL glow peaks of thermally treated specimens, along the OSL decay for the identical physical treatments significant findings were reported. These findings were also corroborated and confirmed with ESR.

Higher temperature of anneal and higher beta doses showed significant changes in TL glow peaks. The higher annealing treatment forms better thermal stability for 220°C TL glow peak. Along with better TL dose response of 220°C glow peak, TL study after optical bleaching showed that the NSQ (Nano Synthetic Quartz) material gives the information about wider family of stable TL traps between 220°C and 235°C. This is attributed to the developed Ge centers at the cost of E_1' centers at higher anneal temperature in NSQ specimens. These findings were clearly confirmed with ESR results also. The higher annealing treatment found be supporting to increase the contribution of usual OSL components outcomes controlling the losses of OSL counts as a rapid decay. Corroborative studies of ESR and XRD also revealed that the thermal treatment affect significantly the centers in nano synthetic quartz specimen. Lower (400°C) annealing temperature is found to be suitable for significant strength in TL and OSL counts in NSQ sample. Such thermally treated NSQ may be the candidate for OSL dosimeter due to better stability of the center.

1.10 References

1 Boetter-Jensen, L. *Development of Optically Stimulated Luminescence Techniques using Natural Minerals and Ceramics, and their Application to Retrospective Dosimetry* PhD thesis, University of Copenhagen, (2000).

2 Wintle, A. G. Luminescence dating: laboratory procedures and protocols. *Radiation Measurements* **27**, 769-817, doi:https://doi.org/10.1016/S1350-4487(97)00220-5 (1997).

3 Gandhi, Y. H., Vyas, P. R. & Joshi, T. R. Trap Level Characterization of Synthetic Quartz. *Crystal Research and Technology* **30**, 1011-1016, doi:doi:10.1002/crat.2170300725 (1995).

4 Kristianpoller, N., Abu-Rayya, M. & Chen, R. The Variation of TL Properties of Synthetic Quartz by Thermal Annealing. *Radiation Protection Dosimetry* **33**, 193-195, doi:10.1093/oxfordjournals.rpd.a080790 (1990).

5 Carvalho Jr, Á. B. d., Guzzo, P. L., Sullasi, H. L. & Khoury, H. J. Effect of particle size in the TL response of natural quartz sensitized by high dose of gamma radiation and heat-treatments. *Materials Research* **13**, 265-271 (2010).

6 Kale, Y. D. & Gandhi, Y. H. Influence of pre-measurement thermal treatment on OSL of synthetic quartz measured at room temperature. *Journal of Luminescence* **128**, 499-503, doi:https://doi.org/10.1016/j.jlumin.2007.09.025 (2008).

7 Ranjbar, A., Durrani, S. & Randle, K. Electron spin resonance and thermoluminescence in powder form of clear fused quartz: effects of grinding. *Radiation measurements* **30**, 73-81 (1999).

8 Yang, X. & McKeever, S. The pre-dose effect in crystalline quartz. *Journal of Physics D: Applied Physics* **23**, 237 (1990).

9 Kale, Y. D. *Optically Stimulated Luminescence Of Synthetic Quartz For Different Protocals And Their Correlation With Thermoluminescence* Ph.D. thesis, The M S University of Baroda, (2005).

10 Bhushan, B. *Springer handbook of nanotechnology*. (Springer-Verlag, 2004).

11 Köhler, M. & Fritzsche, W. *Nanotechnology: an introduction to nanostructuring techniques*. (John Wiley & Sons, 2008).

12 Toyoda, S., Rink, W., Schwarcz, H. & Rees-Jones, J. Crushing effects on TL and OSL on quartz: relevance to fault dating. *Radiation Measurements* **32**, 667-672 (2000).

13 Carvalho Jr, Á. B. d., Guzzo, P. L., Sullasi, H. L. & Khoury, H. J. Effect of particle size in the TL response of natural quartz sensitized by high dose of gamma radiation and heat-treatments. *Materials Research* **13**, 265-271 (2010).

14 Siti Shafiqah, A. S., Amin, Y. M., Nor, R. M. & Bradley, D. A. Effect of particle size on the thermoluminescence (TL) response of silica nanoparticles. *Radiation Physics and Chemistry* **117**, 102-107, doi:https://doi.org/10.1016/j.radphyschem.2015.08.004 (2015).

15 Rivera, T. Synthesis and thermoluminescent characterization of ceramics materials. *Advances in ceramics–synthesis and characterization, processing and specific applications. InTech, Rijeka, Croatia*, 127-164 (2011).

16 McKeever, S. W. *Thermoluminescence of solids*. Vol. 3 (Cambridge University Press, 1988).

17 Bøtter-Jensen, L. *Development of optically stimulated luminescence techniques using natural minerals and ceramics, and their application to retrospective dosimetry*. (Risø National Laboratory, 2000).

18 Koul, D. 110° C thermoluminescence glow peak of quartz—A brief review. *Pramana* **71**, 1209-1229 (2008).

19 Zala, P. P. *Luminescence study of dolomite mineral*, Saurashtra University, (2012).

20 Bøtter-Jensen, L. Development of optically stimulated luminescence techniques using natural minerals and ceramics, and their application to retrospective dosimetry. (2000).

21 Özgen, C. *Optically stimulated luminescence studies on natural fluorites*, MIDDLE EAST TECHNICAL UNIVERSITY, (2011).

22 Bøtter-Jensen, L., McKeever, S. W. & Wintle, A. G. *Optically stimulated luminescence dosimetry*. (Elsevier, 2003).

23 Kitis, G., Liritzis, I. & Vafeiadou, A. Deconvolution of optical stimulated luminescence decay curves. *Journal of Radioanalytical and Nuclear Chemistry* **254**, 143-149 (2002).

24 McKeever, S. & Chen, R. Luminescence models. *Radiation Measurements* **27**, 625-661 (1997).

25 Smith, B. & Rhodes, E. Charge movements in quartz and their relevance to optical dating. *Radiation Measurements* **23**, 329-333 (1994).

26 McKeever, S., Bøtter-Jensen, L., Larsen, N. A. & Duller, G. Temperature dependence of OSL decay curves: experimental and theoretical aspects. *Radiation Measurements* **27**, 161-170 (1997).

27 McKeever, S. W. Optically stimulated luminescence dosimetry. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **184**, 29-54 (2001).

28 Daniels, F., Boyd, C. A. & Saunders, D. F. Thermoluminescence as a Research Tool. *Science (New York, N.Y.)* **117**, 343-349, doi:10.1126/science.117.3040.343 (1953).

29 Aitken, M. J., Tite, M. S. & Reid, J. Thermoluminescent Dating of Ancient Ceramics. *Nature* **202**, 1032, doi:10.1038/2021032b0 (1964).

30 Aitken, M. J., Zimmerman, D. W. & Fleming, S. J. Thermoluminescent Dating of Ancient Pottery. *Nature* **219**, 442, doi:10.1038/219442a0 (1968).

31 MEJDAHL, V. THERMOLUMINESCENCE DATING OF ANCIENT DANISH CERAMICS. *Archaeometry* **11**, 99-104, doi:doi:10.1111/j.1475-4754.1969.tb00632.x (1969).

32 Wintle, A. G. & Huntley, D. J. Thermoluminescence dating of ocean sediments. *Canadian Journal of Earth Sciences* **17**, 348-360, doi:10.1139/e80-034 (1980).
33 Aitken, M. J. *Thermoluminescence Dating*. (Academic Press, 1985).
34 Durrani, S. A., Khazal, K. A. R., McKeever, S. W. S. & Riley, R. J. Studies of changes in the thermoluminescence sensitivity in quartz induced by proton and gamma irradiations. *Radiation Effects* **33**, 237-244, doi:10.1080/00337577708233112 (1977).
35 Sunta, M. D. a. C. M. Thermoluminescence of quartz - Part VI: effect of ultraviolet rays. *Indian Journal of Pure and Applied Physics* **19**, 1041-1047 (1981).
36 Hornyak, A. D. F. a. W. F. Isolation of the rapidily bleaching peak in quartz TL glow curves. *Ancient TL* **8**, 29-31 (1990).
37 Malik, D. M., Kohnke, E. E. & Sibley, W. A. Low-temperature thermally stimulated luminescence of high quality quartz. *Journal of Applied Physics* **52**, 3600-3605, doi:10.1063/1.329092 (1981).
38 Huntley, D. J., Godfrey-Smith, D. I., Thewalt, M. L. W., Prescott, J. R. & Hutton, J. T. Some quartz thermoluminescence spectra relevant to thermoluminescence dating. *International Journal of Radiation Applications and Instrumentation. Part D. Nuclear Tracks and Radiation Measurements* **14**, 27-33, doi:https://doi.org/10.1016/1359-0189(88)90038-6 (1988).
39 Miallier, D. *et al.* Properties of the red TL peak of quartz relevant to thermoluminescence dating. *International Journal of Radiation Applications and Instrumentation. Part D. Nuclear Tracks and Radiation Measurements* **18**, 89-94, doi:https://doi.org/10.1016/1359-0189(91)90098-3 (1991).
40 Krbetschek, M. R., Götze, J., Dietrich, A. & Trautmann, T. Spectral information from minerals relevant for luminescence dating. *Radiation Measurements* **27**, 695-748, doi:https://doi.org/10.1016/S1350-4487(97)00223-0 (1997).
41 Franklin, A. D., Prescott, J. R. & Robertson, G. B. Comparison of blue and red TL from quartz. *Radiation Measurements* **32**, 633-639, doi:https://doi.org/10.1016/S1350-4487(00)00050-0 (2000).
42 Zimmerman, J. The radiation-induced increase of the 100 C thermoluminescence sensitivity of fired quartz. *Journal of Physics C: Solid State Physics* **4**, 3265 (1971).
43 Chen, R., Yang, X. H. & McKeever, S. W. S. The strongly superlinear dose dependence of thermoluminescence in synthetic quartz. *Journal of Physics D: Applied Physics* **21**, 1452 (1988).
44 Rendell, H. M., Townsend, P. D., Wood, R. A. & Luff, B. J. Thermal treatments and emission spectra of TL from quartz. *Radiation Measurements* **23**, 441-449, doi:https://doi.org/10.1016/1350-4487(94)90077-9 (1994).
45 Benny, P. G. & Bhatt, B. C. Sensitization of 220°C TL peak in quartz separated from sand. *Radiation Measurements* **27**, 67-69, doi:https://doi.org/10.1016/S1350-4487(97)00001-2 (1997).
46 Kitis, G., Pagonis, V., Carty, H. & Tatsis, E. Detailed Kinetic Study of the Thermoluminescence Glow Curve of Synthetic Quartz. *Radiation*

Protection Dosimetry **100**, 225-228, doi:10.1093/oxfordjournals.rpd.a005852 (2002).

47 Charitidis, C., Kitis, G., Furetta, C. & Charalambous, S. Superlinearity of Synthetic Quartz: Dependence on Pre-Dose. *Radiation Protection Dosimetry* **84**, 95-98, doi:10.1093/oxfordjournals.rpd.a032806 (1999).

48 Charitidis, C., Kitis, G., Furetta, C. & Charalambous, S. Superlinearity of synthetic quartz: Dependence on the firing temperature. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **168**, 404-410, doi:https://doi.org/10.1016/S0168-583X(99)01199-4 (2000).

49 Benny, P. G., Gundu Rao, T. K. & Bhatt, B. C. The E_1'-centre and its role in TL sensitization in quartz. *Radiation Measurements* **35**, 369-373, doi:https://doi.org/10.1016/S1350-4487(02)00064-1 (2002).

50 Y S Horowitz. *Thermoluminescence and thermoluminesent Dosimetry*. Vol. I (Boca Raton, FL; CRC Press, 1984).

51 Toyoda, S., Rink, W. J., Schwarcz, H. P. & Rees-Jones, J. Crushing effects on TL and OSL on quartz: relevance to fault dating. *Radiation Measurements* **32**, 667-672, doi:https://doi.org/10.1016/S1350-4487(00)00088-3 (2000).

52 Benny, P., Shah, M., Sabharwal, S., Bhatt, B. & Gundu, R. Dosimetric characterization and identification of TL defect centres in sand for its application in sludge irradiators as an in situ dosimeter. (Bhabha Atomic Research Centre, 2003).

53 Huntley, D. J., Godfrey-Smith, D. I. & Thewalt, M. L. W. Optical dating of sediments. *Nature* **313**, 105, doi:10.1038/313105a0 (1985).

54 Bøtter-Jensen, L. & Duller, G. A. T. A new system for measuring optically stimulated luminescence from quartz samples. *International Journal of Radiation Applications and Instrumentation. Part D. Nuclear Tracks and Radiation Measurements* **20**, 549-553, doi:https://doi.org/10.1016/1359-0189(92)90003-E (1992).

55 Bøtter-Jensen, L., Jungner, H. & Mejdahl, V. Recent Developments of OSL Techniques for Dating Quartz and Feldspars. *Radiation Protection Dosimetry* **47**, 643-648, doi:10.1093/oxfordjournals.rpd.a081824 (1993).

56 L Bøtter-Jensen, S. W. S. M., A G Wintle. *Optically Stimulated Luminescence Dosimetry*. (Elsevier, 2003).

57 McKeever, S. W. S. Thermoluminescence in Quartz and Silica. *Radiation Protection Dosimetry* **8**, 81-98, doi:10.1093/oxfordjournals.rpd.a083044 (1984).

58 McKeever, S. W. S. & Chen, R. Luminescence models. *Radiation Measurements* **27**, 625-661, doi:https://doi.org/10.1016/S1350-4487(97)00203-5 (1997).

59 Kale, Y. D., Gandhi, Y. H. & Gartia, R. K. Dose-dependent optically stimulated luminescence of synthetic quartz at room temperature. *Journal of Luminescence* **128**, 1913-1916, doi:https://doi.org/10.1016/j.jlumin.2008.05.023 (2008).

60 Franklin, A. D., Prescott, J. R. & Scholefield, R. B. The mechanism of thermoluminescence in an Australian sedimentary quartz. *Journal of*

Luminescence **63**, 317-326, doi:https://doi.org/10.1016/0022-2313(94)00068-N (1995).
61 Wintle, A. G. & Murray, A. S. A review of quartz optically stimulated luminescence characteristics and their relevance in single-aliquot regeneration dating protocols. *Radiation Measurements* **41**, 369-391, doi:https://doi.org/10.1016/j.radmeas.2005.11.001 (2006).
62 Wintle, A. G. & Murray, A. S. The relationship between quartz thermoluminescence, photo-transferred thermoluminescence, and optically stimulated luminescence. *Radiation Measurements* **27**, 611-624, doi:https://doi.org/10.1016/S1350-4487(97)00018-8 (1997).
63 Bailey, R. M., Smith, B. W. & Rhodes, E. J. Partial bleaching and the decay form characteristics of quartz OSL. *Radiation Measurements* **27**, 123-136, doi:https://doi.org/10.1016/S1350-4487(96)00157-6 (1997).
64 Murray, A. S. & Wintle, A. G. Factors controlling the shape of the OSL decay curve in quartz. *Radiation Measurements* **29**, 65-79, doi:https://doi.org/10.1016/S1350-4487(97)00207-2 (1998).
65 Godfrey-Smith, D. I., Huntley, D. J. & Chen, W. H. Optical dating studies of quartz and feldspar sediment extracts. *Quaternary Science Reviews* **7**, 373-380, doi:https://doi.org/10.1016/0277-3791(88)90032-7 (1988).
66 Rees-Jones, J. Optical Dating of young sediments using fine –grain quartz. *Ancient TL* **13** (1995).
67 Lowick, S. E., Preusser, F. & Wintle, A. G. Investigating quartz optically stimulated luminescence dose–response curves at high doses. *Radiation Measurements* **45**, 975-984, doi:https://doi.org/10.1016/j.radmeas.2010.07.010 (2010).
68 Preusser, F. *et al.* Quartz as a natural luminescence dosimeter. *Earth-Science Reviews* **97**, 184-214 (2009).
69 Bailey, R. The slow component of quartz optically stimulated luminescence. *Radiation Measurements* **32**, 233-246 (2000).
70 Gong, Z., Sun, J. & Lü, T. Investigating the components of the optically stimulated luminescence signals of quartz grains from sand dunes in China. *Quaternary Geochronology* **29**, 48-57 (2015).