3.1 Material

Large amount of work has been done in micron sized of phosphors but now at present nano material has great attraction due to its improved optical properties.Materials in nano-meter size 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. The desirability criteria of a nonmaterial are its submicron size, narrow size distribution, high level of dispersibility and low extent of agglomeration[3]. Nanoparticles of natural quartz have been prepared and their optical properties have been studied[4] by several workers. Therefore, in present work, nano sized synthetic quartz is prepared for the OSL and TL study under different physical conditions for the purpose of dosimetry and dating applications. Laboratory grown synthetic quartz was supplied by Center of Glass and Ceramic Research Institute (CGCRI), Kolkata. This crystal was prepared using hydrothermal technique. In this chapter, general descriptions of instruments employed and different experimental methods being used are discussed in detail.

3.2 Instruments

The following instruments were used in the preparation and characterization of the nano-sized synthetic quartz:

1. Planetary high energy ball mill (FRITSCH Planetary Mono Mill PULVERISETTE 6 Classic Line, Germany)
2. Weighing balance (AX120, Shimadzu, Japan)
3. Bath Sonicator
4. Beta Radiation Source
5. Muffle Furnace
6. Energy dispersive X-ray spectroscopy (EDS JELO MODEL JSM5810LV)
7. UV-visible Spectrophotometer (UV-1700, Shimadzu, Japan)
8. Spectro fluoro photometer (RF-5301, Shimadzu, Japan)
9. Particle Size Analyzer (Malvern Zetasizer Nano ZS 90, Malvern Instruments, UK)
10. X-ray Diffractometer (XRD, X-Pert-PRO, PANalytical, Netherland)
11. Bruker ALPHA FTIR Spectrometer (Bruker Optics, Germany)

12. Scanning Electron Microscope (SEM, JSM-6060, JEOL Ltd., Tokyo, Japan)
13. Transmission Electron Microscope (TEM, PHILIPS, Technai 20, Japan)
14. Risø TL/OSL Reader (model TL/OSL-DA-20)
15. ESR-Varian, USA (E-112 ESR Spectrometer)

3.3 Preparation of nano sized synthetic quartz (NSQ) sample

Various methods have been used for preparation of ceramic or metal nanoparticles such as mechanical alloying, combustion synthesis, plasma forming, explosive forming, electro deposition, sol-gel technique and media milling/ball milling process[1,6,7]. Among these methods, high energy ball milling (BM) is favourable technique hence widely used in production of nano particles due to its simplicity, user friendly operation, low cost of production and applicability to any class of materials at large quantities[8]. Several workers have used BM method for the synthesis of nano-particles of different materials like Fe_2O_3-SnO_2, ZrO_2-Fe_2O_3, TiO_2-Fe_2O_3, TiO_2-WO_3, SiC, Si_3N_4 and quartz (SiO_2)[9,10]. Micron-sized synthetic quartz samples were prepared by top to down approach (method) using mortar-pestle and sieving. To follow BM method, micron-sized sample was used as a starting material in ball mill for further size reduction to nano-metric level in present work.

3.3.1 High energy Planetary Ball Mill Technique

One of the high energy ball mills is planetary ball mill. In this mill arrangement, the milling jar is arranged in such a way that it is eccentrically set on a sun wheel of the ball mill, with the direction of the rotation of the sun wheel being opposite to that of the milling jar (Fig. 3.1).

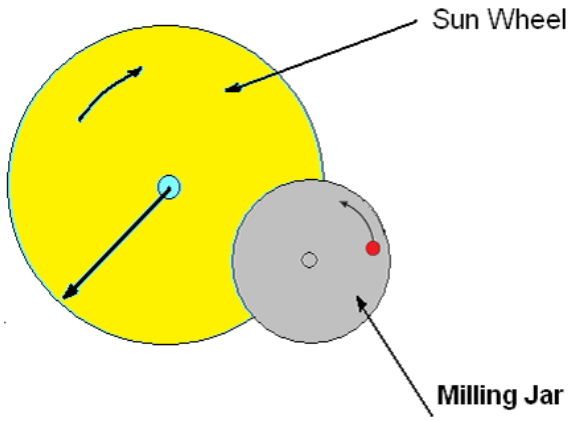

Fig 3.1 Arrangement of milling jar with sun wheel[11].

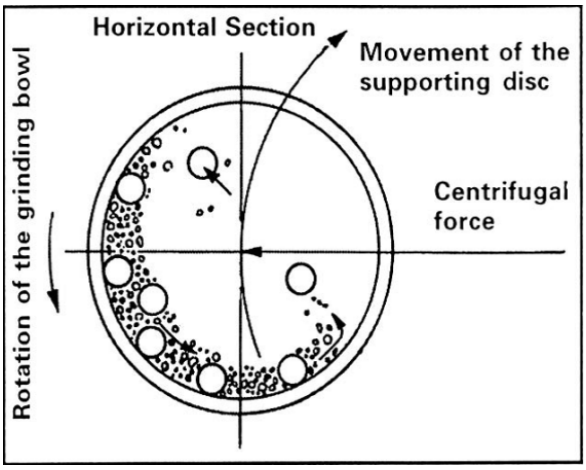

Fig. 3.2 The ball motion inside the milling jar and acting force on ball[11].

Planetary ball mills work on the principle of centrifugal acceleration instead of gravitation acceleration. During milling, inside the milling jar, the centrifugal forces alternately act in opposite directions not only prevent milling balls from being pinned to inside wall of the jar but the force also reasons the milling balls to run down the inside wall (Fig. 3.2). This generates a friction crushing effect followed by the balls lifting and flying to other side of the jar. As a result, they collide and give impact of crushing effects[11].

3.3.2 Preliminary optimization of the parameters for sample preparation

Prior to the sample preparation step, the possible parameters influencing the preparation of nano sized particles, the size of nanoparticles were identified and optimized. The effect of parameters was observed by varying one

parameter at a time and keeping other constant so that selected parameter could be optimized. The parameters were optimized to minimum mean particle size and poly dispersity index (PDI). Performed trials are enlisted below:

Trial 1: Variation in milling ball diameters

Trial 2: Use of different dispersing mediums

Trial 3: Variation in surfactant concentration

Trial 4: Variation in ball to powder weight ratios

Trial 5: Variation in milling time

3.3.3 Thermal Annealing Treatment

The phase transformation of α to β at 573^{o}C and β to tridymite at 873^{o}C is well established in synthetic quartz due to structure sensitive dynamics of material under the influence of temperature. Such phase transformation are responsible for the changes in TL and OSL sensitivity[12]. With this view; such nano sized samples were divided into two parts. One part was named as "un annealed" samples and second part as "annealed" samples. For annealing treatment, nano-sized synthetic quartz specimens were transferred to a silica crucible and kept in the programmable muffle furnace which was having the temperature range up to 1200°C. The samples were heated separately in muffle furnace to give different pre heat treatment at annealing temperatures such as 400°C, 600°C and 1000°C for 1 hour duration. After completion of pre set annealing duration, samples were took out from furnace and brought directly to the room temperature for quenching.

3.3.4 Irradiation Treatment

Sr^{90} Beta radiation source with calibrated dose rate 7.88Gy/min was used as ionizing radiation in the Risø TL/OSL reader. Unannealed and annealed samples of nano synthetic quartz were irradiated for different beta radiation doses which are as follows: 15.76Gy, 48.03Gy, 81.43Gy, 120.83Gy, 160.23Gy, and 199.63Gy.

3.4 Characterization of Nano sized Sample

The prepared nano sized synthetic quartz sample was characterized by Particle size analyzer, SEM, TEM, XRD,EDX and FTIR for detection of impurity, contamination, morphology and particle size. UV-visible spectroscopy was used for the information about absorption wavelength of the prepared samples whereas, PL spectra revealed information about emission wavelength of the prepared samples.

3.4.1 Particle Size Analysis

The particle size (PS) and polydispersity index (PDI) of prepared ball milled synhtetic quartz samples were measured using Malvern Zetasizer Nano ZS 90 (Malvern Instruments, Worcestershire, UK), which follows principle of LASER Diffraction (LD) using Photon correlation spectroscopy (PCS). Photon correlation spectroscopy is based on the measurement of the Brownian motion of particles[13]. Samples were suitably diluted with double distilled water before measurement, to avoid multiple scattering. Detection was carried out at a scattering angle of 90°; sample temperature was set at 25°C and 12-17 runs of 30 seconds were performed on each sample. Six replicates of each sample were measured. The average particle size and PDI were measured.

3.4.2 Scanning Electron Microscopy (SEM) Analysis

Scanning electron microscopy scan of the sample with focused electron beam produce images with the information about the topography and morphology of the samples[14]. SEM spectra suggest the confirmation about proposed size of the particles which are going to be used.

The morphology of the prepared synthetic quartz nanoparticles were observed using a Scanning Electron Microscope 205 (SEM, JSM-5610, JEOL Ltd. Tokyo, Japan). The specimen was placed directly on the SEM sample holder using double-sided sticking carbon tape and images were captured at 15 kV acceleration voltage at the required magnification[15].

3.4.3 Transmission electron Microscopy (TEM) Analysis

In TEM analysis, high energy electrons are used to provide morphologic, compositional and crystallographic information of samples. TEM is a powerful

microscope and it has one nanometer potential of magnification. Electrons are scattered when an electron beam passes through a thin part of a sample. A system of electromagnetic lenses focuses the scattered electrons into an image or a diffraction pattern, or a nano-analytical spectrum, which are depending upon the mode of operation. A different vision and a highly magnified view of the micro- and nanostructure was examined by each of these imaging mode of TEM[14].

In present study, the morphological investigations of optimized nano-synthetic quartz samples were carried out by using a Transmission Electron Microscope (TEM PHILIPS, Technai-20, Japan). For TEM investigation, a known concentration (0.5mg/ml) of synthetic quartz nano-suspension (SQ-NS) in water was prepared. A drop of SQ-NS was placed on a coated carbon grid (300 mesh, 3mm) and air dried. The grid was then examined immediately under Transmission Electron Microscope. The electron micrographs were obtained after magnifications.

3.4.4 X-Ray Diffraction (XRD) Analysis

XRD is a technique to measure crystalline structure, crystalline size, lattice constants, composition of solid solution and degree of crystallinity in a mixture of amorphous and crystalline substances. X-ray diffraction is dependent on the constructive interference of the X-ray and sample. When condition of Bragg's law is satisfied, then interaction between incident ray and sample produce constructive interference. These diffracted X-rays are detected by detector[16].

X-ray diffraction (XRD) using an X-ray Diffractometer (XRD, X-Pert-PRO, PANalytical, Netherland) with CuKα, operating at 45kV and 40 mA characterized the prepared samples. The sample was mounted on a sample holder and XRD pattern was recorded in the range of $15^o < 2\theta < 80^o$ at the speed of 5^o min^{-1}.The crystallite size of the milled powder was determined by X-ray line broadening and calculated using the Scherrer Equation[17] 3.1.

$$d = \frac{0.91\lambda}{\beta \cos\theta} \qquad \text{Eq.3.1}$$

Where d is the mean grain size, β is the full width at half maximum (FWHM). θ is the angle of the peak maximum, and λ (0.15406nm) is the Cu(Kα) wavelength.

3.4.5 Energy Dispersive X-ray spectroscopy (EDS/EDX) Analysis

Energy dispersive X-ray spectroscopy (EDS, EDX, or XEDS) is an analytical tool used to analyse a sample's elemental or chemical characterization. It depends on interaction of some source of X-ray excitation and a sample. In this technique, electron beam collide with the sample, exciting an electron in an inner shell, causing its ejection and creation of an electron hole in the electronic structure of the element[18].

Nano-sized synthetic quartz sample prepared by ball mill process may comprise of metallic contamination or many other process related impurities which may affect the luminescence properties of the material. Therefore, energy dispersive X-ray spectroscopy (EDS JELO MODEL JSM5810LV) study was undertaken to detect any contamination/in-process impurity and to confirm elemental composition in prepared nano-sized synthetic quartz samples.

3.4.6 Fourier Transfer Infrared Spectroscopy (FTIR) Study

FTIR spectroscopy is most suitable technique for identification of the chemicals that may be organic or inorganic. It depends on the fact that the most molecules absorb light in the infra-red region of the electromagnetic spectrum. This absorption relates precisely to the bond present in the molecule. The frequency range with wave number typically is in the range of 4000-600cm^{-1}. In present work, FTIR was performed for identification of induced defects in synthetic quartz due to milling the sample and chemical species through the analysis of vibration bands, where positively charged hydrogen atom are involved. These impurities and defects assist as non-radiative recombination centre or as trapping centres to compete with radiative recombination centres during luminescence processes. The hydroxides worked as hole scavengers as reported in studies of metal oxides[19].

The Prepared nano-sized sample of synthetic quartz was characterized by Fourier transfer infrared spectroscopy using Bruker ALPHA FTIR Spectrometer (Bruker Optics, Germany) for examination of the impurities and defects in the sample.Spectra was recorded over a spectral region from 4000 cm^{-1} to 600 cm^{-1} with resolution 4 cm^{-1} and 100 scans.

3.4.7 UV-Visible spectroscopy study

UV-Visible spectroscopy is a simple, sensitive and accurate technique for the measurement of absorbance or transmittance of the sample from UV – Visible range. When a light with sufficient energy and wavelength is incident on the sample, some part of energy of incident light is absorbed by the sample during transmission. The energy of light is transmitted from the sample after that, it is measured by using photo detector, which accounts as the absorbance of the sample. UV-Visible spectra is a graphical depiction of the amount of light absorbed or transmitted by material as a function of wavelength[20].

UV-Visible-double beam spectrometer (UV-1800 Shimadzu, Japan) with defined slit width (2nm) was used for all absorbance measurements of prepared nano-sized samples using 1.0 cm matched quartz cells.

10mg weight of micron sized sample was transferred into 100 ml distilled water to prepare a test solution for the measurement of absorbance. This solution was stirred for 30 minutes for complete dispersion of particles into distilled water. The analysis was performed by first scanning test solution under the UV-visible range between 200-800 nm using distilled water as blank and determined its absorbance maxima (λ_{max}). This procedure was followed for all nano sized samples (Un-annealed and annealed).

3.4.8 Photoluminescence study

Photoluminescence spectroscopy is a simple, multipurpose, contactless and non-destructive technique to investigate the electronic structure of materials. When light of sufficient energy is directed onto a sample, photons are absorbed, and electron excitation took place. Excited electron returned into the ground state after relaxation. If these relaxations are radiative, then emitted light is called photoluminescence (PL). PL is referred as an 'intra-centre' transition phenomenon and it does not involve the delocalization of electrons or holes. Hence PL is the spontaneous emission of light from a material under optical excitation. This light is collected on detector and investigated spectrally, spatially and temporally. PL intensity and spectrum, both content provide the direct information about the various important properties of the material[21].

PL emission spectra of prepared man-sized synthetic quartz samples were measured with excitation wavelength at 220nm using Spectrofluorophotometer (RF-5301 Shimadzu, Japan).

3.4.9 Thermoluminescence Analysis

Thermo luminescence phenomenon is well described in Section 1.4.TL glow curve of prepared nano (unannealed and annealed) synthetic quartz samples followed by different beta doses were recorded from 0 to 398°C with 2°Cs^{-1} constant heating rate by using Risø TL/OSL reader (model TL/OSL-DA-20). TL intensity was normalized by weight for each sample.

3.4.10 Optically Stimulated Luminescence Analysis

Optically Stimulated Luminescence phenomenon is well described in Section 1.5. The phenomenon of optically stimulated luminescence is directly related to electron traps in semiconductors or insulators which occurred due to the presence of point defects in the crystal structure. In OSL phenomenon, radiation dose is used to transfer the carriers into trap levels. These concentrations of trapped electrons are directly proportional to the OSL intensity. Therefore, the relation between absorbed radiation dose by a phosphor and the OSL intensity is widely used for dosimetry[22,23]. In present study, Continuous Wave OSL (CWOSL) is used for OSL measurement. For the CWOSL measurement, a simple decay curve is observed when optical stimulation is performed with light of constant wavelength and constant intensity.

OSL decay curve of prepared nano synthetic quartz samples(un-annealed and annealed) were recorded for 0 to 100 sec at room temperature by using Risø TL/OSL reader (model TL/OSL-DA-20) having 470 nm laser line or broad band stimulation wavelength. OSL intensity was normalized by weight for each sample. OSL decay curve is explained through the components. ORIGIN8.0 software is used to resolve the OSL components by operating exponential decay curve fitting method and slope resolved by linear fit of OSL intensity within decay time 0 to 0.4 sec.

3.4.11 Electron Spin Resonance (ESR) Analysis

ESR is one of the branches of absorption spectroscopy in which radiation has frequency in the microwave region (0.04-25cm). In this process, radiation is absorbed by paramagnetic substances to persuade transitions between magnetic energy level of electrons with unpaired spins. This absorption of microwave radiation takes place under the influence of an applied magnetic field. The paramagnetic substances are having one or more unpaired electrons and so, they exhibit ESR. ESR is also known as electron paramagnetic resonance (EPR)[24].

Each electron has magnetic moment and spin quantum number $s = 1/2$ along with magnetic components $m_s = +1/2$ and $m_s = -1/2$.If external magnetic field with strength B_0 is present, then, the electron's magnetic moment aligns itself either parallel or anti parallel to the field. Every alignment having a specific energy due to the Zeeman Effect:

$$E = m_s g_e \mu_B B_0 \qquad \text{Eq. 3.2}$$

Where, $g_e$is Lande g-factor of electrons and μ_B is Bohr magneton.Hence, the difference between lower and upper state $\Delta E = g_e \mu_B B_0$is used to calculate g-factor for unpaired free electron. The g-factor give the information about electronic structure of a paramagnetic centre. Above equation shows that split of energy levels (ΔE) is directly propotional to external magnetic field with (B_0) strength[24] (Fig. 3.3).

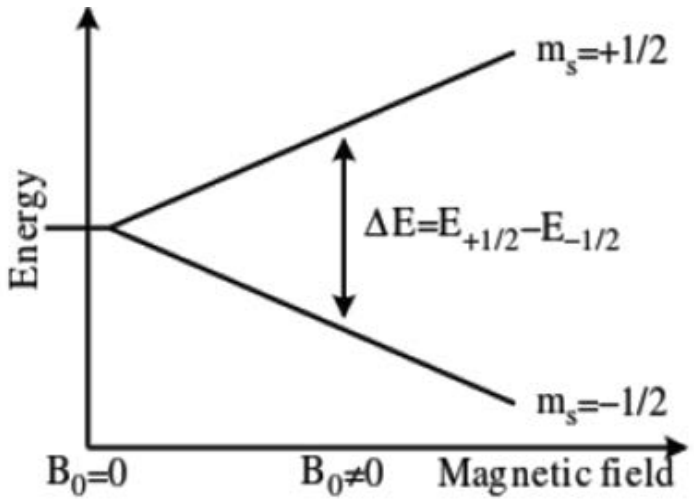

Fig. 3.3 Energy levels of unpaired free electron with respect to applied magnetic field[24].

In present study, ESR signal was used to detect the defect centre present in the material which helped to confirm and explain the changes observed in TL and OSL behaviour of the nano synthetic quartz under different physical conditions.

Following protocols were used for ESR Study of nano synthetic quartz (NSQ) for different doses and different annealed temperature:

1) Unannealed NSQ + 55Gy beta dose + ESR
2) Unannealed NSQ + 200Gy beta dose + ESR
3) Annealed NSQ at 400°C; 1hr + 55Gy beta dose + ESR
4) Annealed NSQ at 400°C; 1hr + 200Gy beta dose + ESR
5) Annealed NSQ at 600°C; 1hr + 55Gy beta dose + ESR
6) Annealed NSQ at 600°C; 1hr + 200Gy beta dose + ESR
7) Annealed NSQ at 1000°C; 1hr + 55Gy beta dose + ESR
8) Annealed NSQ at 1000°C; 1hr + 200Gy beta dose + ESR

Different ESR spectra of prepared samples were recorded at room temperature using Varian E-112, USA ESR spectrometer with 100 kHz field modulation and 5mW microwave power. Tetracynoethylene (TCNCE, g= 2.00277) is used as a standard for the g-factor measurement.

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