4.1 Introduction

This part of the research work has been aimed to explain process of developing nano sized synthetic quartz (NSQ) by using ball milling method. Further, investigations of optical properties, surface morphology, FTIR spectroscopy etc are being presented for such NSQ specimens with a view to understand TL and OSL property of nano sized synthetic quartz material. Pre-micronized synthetic quartz sample was used as a staring material for the preparation of nano-sized synthetic quartz. Different parameters (milling ball diameter, dispersing medium, surfactant concentration, milling time, ball to powder weight ratio) were tried in an effort to develop nano size sample.The prepared sample was collected in the form of powder and characterized by using Particle Size Analyzer, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM),X-ray Diffraction (XRD) Study, Fourier Transform Infrared Spectroscopy (FTIR),Energy Dispersive X-ray spectroscopy (EDS/EDX) for various investigations. The powdered sample was divided into four parts. One portion was kept untreated, whereas remaining three portions were thermally treated at three different temperatures 400°C, 600°C and 1000°C. The annealed samples were also characterized by XRD to check the phase transformation in nano-synthetic quartz. Optical Absorption of the radiation wavelength by the prepared nano sample was examined with the help of UV-Visible spectroscopy. Emission spectral wavelength was observed by photoluminescence emission spectra. Details of preparation and characterization of the nano-sized sample is given below:

4.2 Nano-sized synthetic quartz sample preparation

High energy ball milling (BM) technique is favourable for Top to Bottom approach, which is widely used in production of nano particles because of its effortlessness, user friendly operation, low cost of production and applicability to any class of materials for production of large quantities[1]. Nano sized synthetic quartz sample was engineered by a high energy planetary ball mill (FRITSCH Planetary Mono Mill PULVERISETTE 6 Classic Line, Germany). In this process; micron sized synthetic quartz was used as starting material, acetone as dispersing medium and Stearic acid as surfactant. Milling jar was made up of tungsten carbide and temperature was maintained at 40°C inside

the jar. Grinding was performed by using tungsten carbide balls as milling media at 350 rpm with ball to powder weight ratio (BPR) 10:1 for total duration of 48 hours. The material produced was washed with dilute HCL followed by distilled water and methanol, to remove process impurities. Then, it was dried in oven at 50°C for 4 hours. The dried sample was used for further investigations[2].

4.2.1 Preliminary optimization of parameters for sample preparation

Prior to the sample preparation step, the possible parameters influencing nano sized particles were identified and optimized. The parameters were optimized by changing one parameter at a time and keeping other parameters constant, so that the effect of 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

4.2.1.1 Variation in Milling Ball Diameters

Tungsten carbide milling balls of three different diameters (i.e. 3mm, 6mm and 10mm) were used for trial, whereas other parameters i.e. dispersing medium (Acetone), volume of dispersing medium (30 ml), surfactant (Stearic Acid), surfactant concentration (2% w/w), BPR (10:1) w/w, rotation speed of milling jar (350 rpm) and milling time (24 hours) were kept constant. The results for particle size of samples obtained by milling with balls having different diameters are summarized in **Table 4.1.**

Table 4.1 Effect of milling ball diameter on average particle size of synthetic quartz.

Sr. No.	Ball Diameter	Average particle size
1.	3 mm	215 nm
2.	**6 mm**	**135 nm**
3.	9 mm	550 nm

Results clearly indicate that maximum size reduction (135 nm) was achieved with balls having diameter of 6 mm and were selected for further media milling.

4.2.1.2 Use of Different Dispersing Mediums

In this trial, water and acetone were used as dispersing medium. Rest of the parameters such as milling ball diameter (6 mm), volume of dispersing medium (30 ml), surfactant (Stearic Acid), surfactant concentration (2% w/w), BPR (10:1 w/w), rotation speed of milling jar (350 rpm) and milling time (24 hours) were kept constant. Observations are presented in **Table 4.2.** In acetone, average particle size achieved was 129 nm and hence acetone was finalized as dispersing medium for further studies.

Table 4.2 Effect of dispersing medium on average particle size of synthetic quartz.

Sr. No.	Dispersing Medium	Average particle size
1.	Water	395 nm
2.	**Acetone**	**129 nm**

4.2.1.3 Variation in Surfactant Concentration

It is an important factor which affects the size reduction of material in media milling. Stearic acid was used as surfactant to evaluate its effectiveness in particle size reduction and stabilization of nano size. Surfactant in three different concentrations (i.e. 1%w/w, 2%w/w and 3%w/w) was used whereas other parameters, milling ball diameter (6 mm), dispersing medium (Acetone), volume of dispersing medium (30 ml), BPR (10:1) w/w, rotation speed of

milling jar (350 rpm) and milling time (24 hours) were kept constant. Obtained results are displayed in **Table 4.3.** Stearic acid at 2% w/w concentration in acetone led to lowest particle size (130 nm) and was found optimum for further experiments.

Table 4.3 Effect of surfactant concentration on average particle size of synthetic quartz.

Sr. No.	Stearic acid concentration	Average particle size
1.	1.0 % w/w	318 nm
2.	**2.0 % w/w**	**130 nm**
3.	3.0 % w/w	180 nm

4.2.1.4 Variation in Ball to Powder Weight Ratio (BPR)

During the course of optimization, three different BPR (i.e. 5:1 w/w, 10:1 w/w and 15:1 w/w) were tried whereas other parameters, milling ball diameter (6 mm), dispersing medium (Acetone), volume of dispersing medium (30 ml), surfactant (Stearic Acid), surfactant concentration (2 %w/w), milling time (24 hrs) and rotation speed of milling jar (350 rpm) were kept constant. Particle size analysis of each trial batch was performed and results were displayed in **Table 4.4**. Results indicated that BPR (10:1 w/w) produced minimum particle size after media milling and hence selected for further trials.

Table 4.4 Effect of variation in BPR on average particle size of synthetic quartz.

Sr. No.	BPR	Average particle size
1.	5:1 w/w	570 nm
2.	**10:1 w/w**	**140 nm**
3.	15:1 w/w	298 nm

4.2.1.5 Variation in Milling Time

In this trial, material was milled for 6 hrs, 12 hrs, 24 hrs, 36 hrs, 48 hrs and 60 hrs. During this trial, milling ball diameter (6 mm), dispersing medium (Acetone), volume of dispersing medium (30 ml), surfactant (Stearic Acid), surfactant concentration (2%)w/w, BPR (10:1) w/w and rotation speed of milling jar (350 rpm) were kept constant. Results of experiment for selection of milling time are shown in **Table 4.5**. Results indicated that minimum particle size (82 nm) was achieved by milling the synthetic quartz for 48 hrs. It could be concluded that duration of milling time employed for preparation of nano synthetic quartz has significant effect on particle size of milled material and appeared to be an important parameter for efficient formation of nano synthetic quartz.

Table 4.5 Effect of variation in milling time on average particle size of synthetic quartz.

Sr. No.	Milling time	Average particle size
1.	06 hrs	490 nm
2.	12 hrs	422 nm
3.	24 hrs	138 nm
4.	36 hrs	113 nm
5.	**48 hrs**	**89 nm**
6.	60 hrs	98 nm

4.2.2 Preparation of optimized nano synthetic quartz

On the basis of preliminary trials, optimized process parameters for preparation of synthetic quartz nanoparticles were chosen as given below:

Milling balls material : Tungsten carbide

Milling ball diameter : 6 mm

Dispersing medium : Acetone

Volume of dispersing medium : 30 ml

Surfactant : Stearic Acid

Surfactant Concentration : 2% w/w

BPR : 10:1 w/w

Milling time : 48 hrs

Rotation speed of milling jar : 350 rpm

The above mentioned process parameters were employed for production of final batch of nano synthetic quartz sample. The average particle size and PDI of produced sample were found to be 87 nm and 0.119, respectively. These nano synthetic quartz specimens were used for further characterizations, physical treatments, and luminescence studies.

4.2.3Thermal and Irradiation Treatment

The prepared nano synthetic quartz sample was divided into four parts. One portion was kept as untreated/ un-annealed, whereas remaining three were thermally treated at three different temperatures, i.e., second, third and fourth parts were annealed at 400°C, 600°C and 1000°C, respectively. Un-annealed and annealed samples of nano synthetic quartz were then irradiated by different beta radiations (dose rate 7.88Gy/min) which are as follows: 15.76 Gy, 48.03 Gy, 81.43 Gy, 120.83 Gy, 160.23 Gy, and 199.63 Gy.

4.3 Characterization of nano sized synthetic quartz sample

The prepared nano sized synthetic quartz samples were characterized by Particle size analyzer, SEM, TEM, EDX, XRD and FTIR for particle size, surface morphology of powdered material, detection of possible impurities and phase transformation due to thermal treatment. UV-visible spectroscopy was used for the information about absorption wavelength of the prepared samples and PL spectra gives information about emission wavelength of the prepared samples.

4.3.1 Particle Size Analysis

Particle size analysis is used to describe size distribution of particle in the sample. Various researchers used this technique to determine particle size of samples, prepared by milling technique[3,4].

Results

		Size (d.nm):	% Intensity	Width (d.nm):
Z-Average (d.nm): 87.0	Peak 1:	92.9	100.0	65.45
PdI: 0.119	Peak 2:	0.000	0.0	0.000
Intercept: 0.877	Peak 3:	0.000	0.0	0.000

Result quality : Good

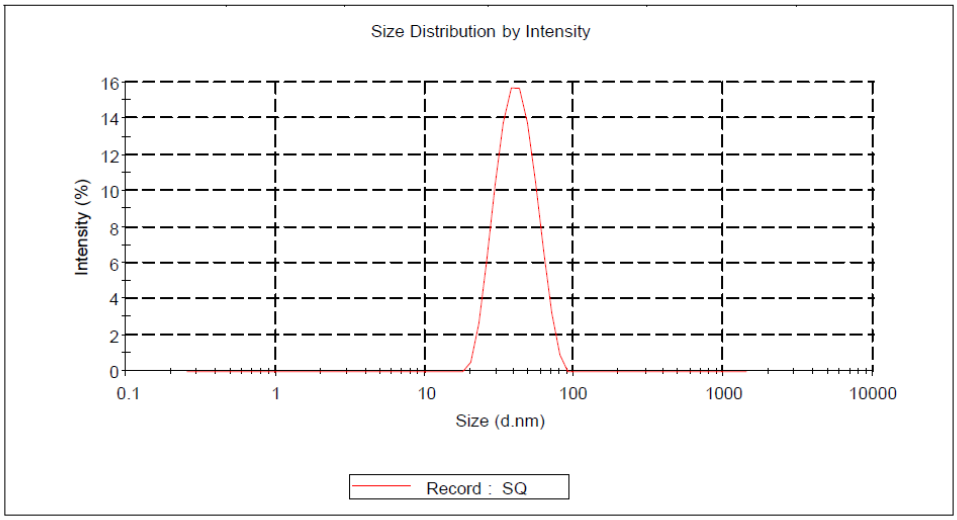

Fig. 4.1 Representation of average particle size and PDI of un-annealed nano synthetic quartz sample

In present study, nano size synthetic quartz from micron sized sample is achieved by planetary ball-milling method. So, particle size and particle size distribution of milled sample is essential to determine by particle size analyzer. From Fig. 4.1, it is observed that the average particle size of prepared nano synthetic quartz sample is 87nm and PDI is 0.119 which shows that maximum particles are in nano-metric range.

4.3.2 Scanning Electron Microscopy (SEM) Study

Researchers tested their inorganic phosphors samples by SEM technique to investigate the size and morphology of the material[5,6]. In present study, un-annealed nano sized synthetic quartz sample was observed by SEM to evaluate size and morphology of particles.

SEM image of the prepared sample is presented in the Fig. 4.2. It can be presented that media milling of micronized synthetic quartz sample in presence of surfactant (citric acid) led to desired size reduction of materials. The actual size of the sample cannot be resolute by SEM due to limits of resolutions of the

instrument but it can be easily foretold that all the particles of the synthetic quartz sample are in nano-metric range. The SEM image also demonstrated that the particles are agglomerated and irregular in shape.

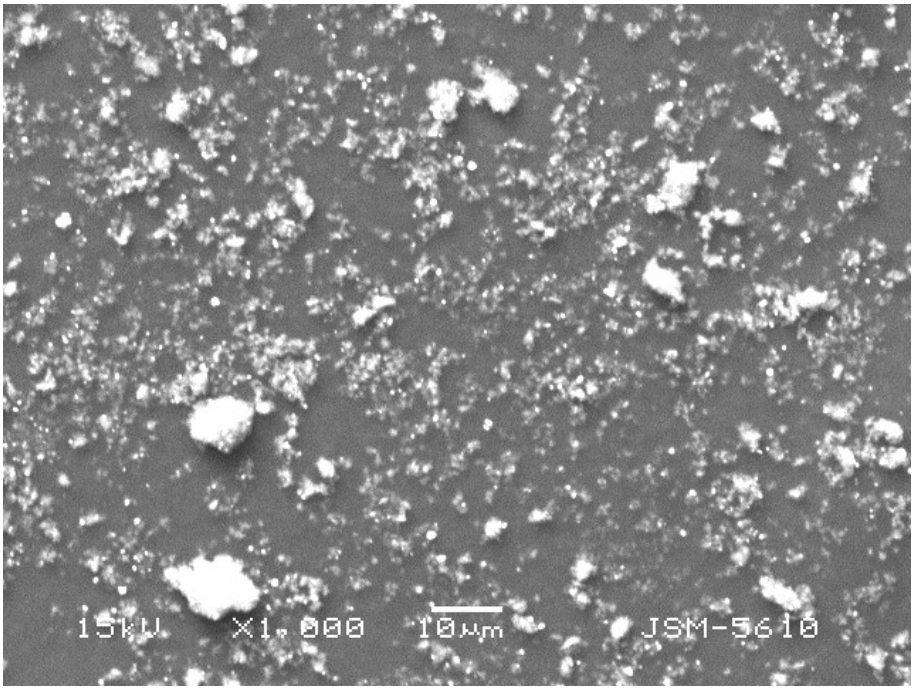

Fig.4.2 SEM image of un-annealed nano synthetic quartz sample.

4.3.3 Transmission electron Microscopy (TEM) study

TEM technique has been used for size and morphological investigations of nano samples of various luminescence phosphors including minerals, organic and inorganic material[3,7]. TEM is a technique used to observe crystallographic and morphological information of the sample. It provides higher resolution images than scanning electron microscopy. In present work, the TEM study was performed for confirmation of particle size in prepared sample. The TEM image of un-annealed nano synthetic quartz sample is presented in Fig. 4.3. The TEM image revealed that the particles are discrete and in nano-metric range and is in very good agreement with particle size obtained by particle size analyzer.

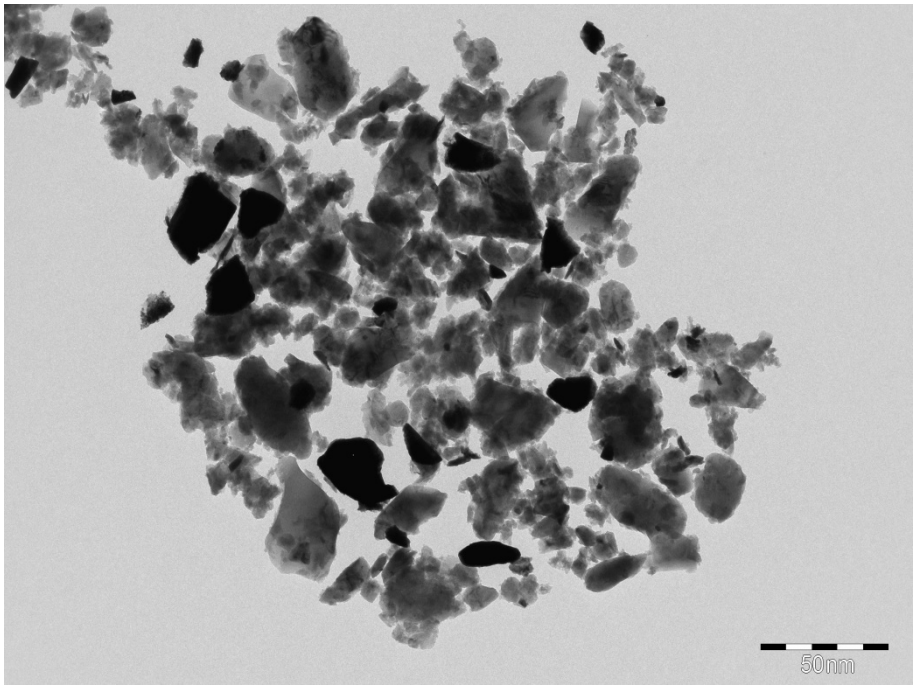

Fig.4.3 TEM image of un-annealed nano synthetic quartz sample.

4.3.4 X-Ray Diffraction (XRD) study

XRD is an essential method for material characterization for surface morphology and it is used to determine crystalline phase, crystalline size and internal stress of small crystalline regions of the various materials. Researcher used XRD to determine crystal structure, crystalline size lattice constant, composition of solid solution and degree of crystallinity in a combination of amorphous and crystalline substances[8]. In present study, XRD study was also carried out to investigate the variation in crystalline state, crystalline size and transformation of phases after annealing of prepared nano synthetic quartz sample at three different temperatures (i.e. 400°C, 600°C & 1000°C). The XRD patterns of un-annealed sample and annealed samples at 400°C, 600°C & 1000°C were recorded and represented in Fig. 4.4 XRD (a), (b), (c) & (d), respectively. The intense sharp peaks observed in diffraction patterns of un-annealed and annealed samples clearly stated that the prepared nano-sample was in crystalline state and remained in the same state after annealing at different temperatures. Average Crystalline size of un-annealed sample was calculated to be 39.41nm from the full width at half maximum (FWHM) of the X-ray diffraction peak using Scherer's equation[9]. In all recorded spectrums, the

peaks centred at 2θ=20.9° and 26.7° with d= 4.25 Å & 3.34 Å, respectively, clearly specified the typical quartz characteristic of sample in α-phase (RRUFF database R040031)[10]. The diffraction spectra of as-received and 400°C annealed nano samples were assigned to quartz trigonal structure which were confirmed by the comparison with JCPDS card no. 46-1045 and RRUFF database (R040031)[10,11]. At a temperature of 400°C, there appears a development of tridymite phase at an angle 23.9° with d=3.71 Å. At 600°C, the strong appearance of peaks at 2θ=23.1°, 23.6° and 24.4° with d=3.83 Å, 3.75 Å and 3.65 Å, respectively, confirmed the emergence of tridymite phase (RRUFF Database R090042). The peaks at angles of 2θ=41.7° and 53.6° with d=2.17 Å and 1.71 Å, respectively, clearly confirmed the occurrence of β-phase at 600°C (Database_code_amcsd_0010604)[12]. Additionally; a peak at 2θ=47.3° with d=1.92 Å showed the presence of cristobalite phase also in the sample annealed at 600°C (RRUFF Database R060648). The XRD spectra of nano synthetic quartz sample annealed at 1000°C, showed sharp intense peaks for maximum presence of tridymite phase at 2θ=23.1°, 23.6° and 24.4° with d=3.83 Å, 3.75 Å and 3.65 Å, respectively (RRUFF Database R090042)[13]. The peaks at 2θ=2.84°, 1.88°, 1.49° and 1.43° with d=31.53 Å, 48.35 Å, 62.28 Å and 65.13 Å, respectively, confirmed the appearance of cristobalite phase at 1000°C (RRUFF Database R060648)[14]. Hence the XRD spectrums of nano sized quartz crystals are also in very good agreement with the well establishment transformation of α-quartz phase into β-quartz, tridymite and cristobalite phases with variation in annealing temperatures. **Table 4.6**, presents the transformation of quartz phases with variation in annealing temperatures.

Table 4.6 Transformation of quartz phases in prepared nano sample with variation in temperatures.

Annealing Temperature	α-Quartz phase	β-Quartz phase	Tridymite phase	Cristobalite phase
Un-annealed	√	---	---	---
400°C	√	---	√	---
600°C	√	√	√	√
1000°C	√	---	√	√

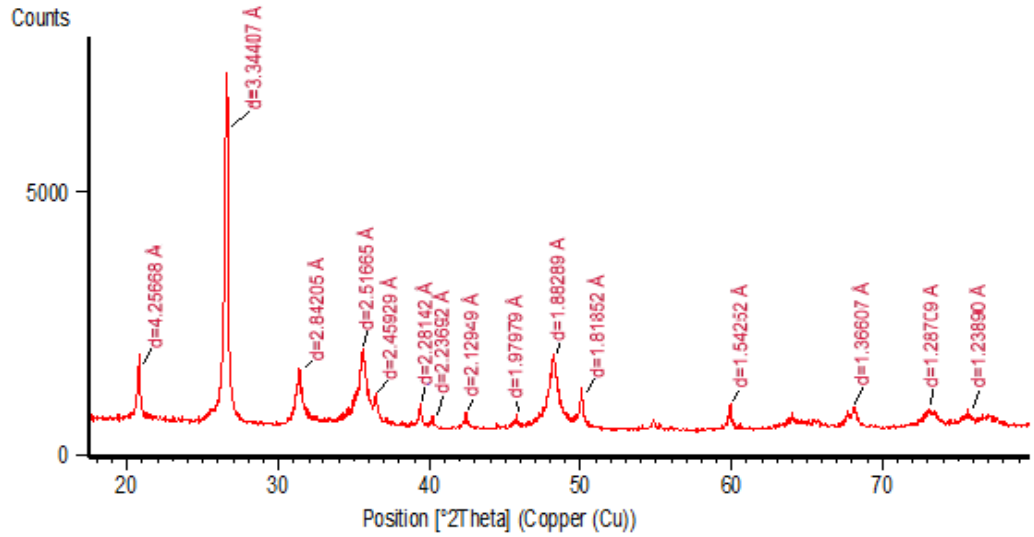

Fig.4.4(a)

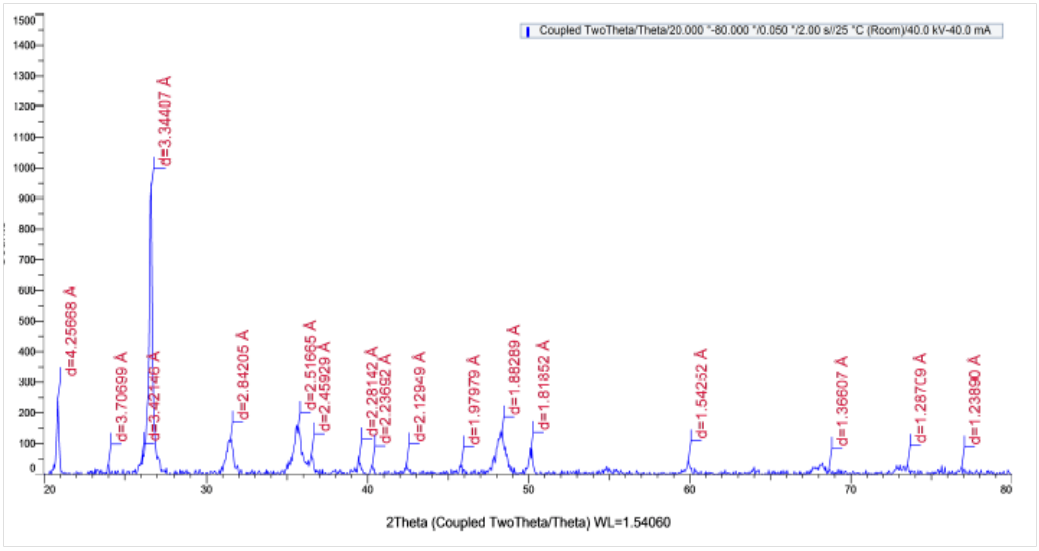

Fig.4.4(b)

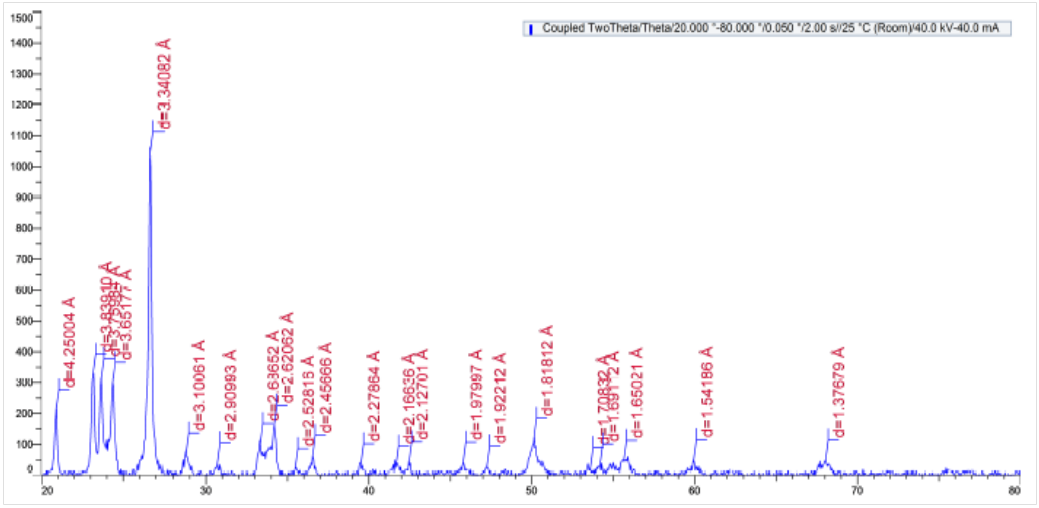

Fig.4.4(c)

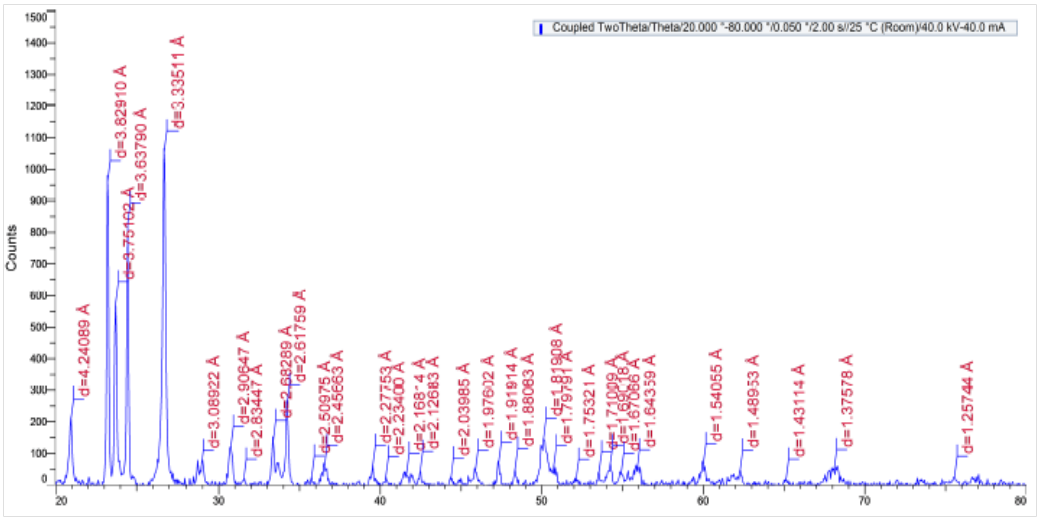

Fig.4.4(d)

Fig.4.4 XRD spectra for prepared **(a)** un-annealed, **(b)** 400°C annealed, **(c)** 600°C annealed and **(d)** 1000°C annealed, nano-sized samples of synthetic quartz.

4.3.5 Electron Diffraction X-ray spectroscopy (EDS/EDX) Study

EDX is an efficient technique to detect and identify impurities which are present in the materials. As discussed earlier that the nano synthetic quartz sample was prepared by ball milling technique using metallic balls and milling jar. During preparation of nano sample, probability of incorporation of process impurity with the material cannot be ignored due to friction between material, ball and milling jar. Considering this fact, it was necessary to detect and investigate the level of impurities in the sample after being sample preparation. EDS study helps to record the signatures of such incorporated impurities. EDS was performed for impurity testing in as such un-annealed nano-sized synthetic quartz material (without chemical treatment) and acid washed (chemical treatment) un-annealed nano-sized synthetic quartz sample. The prepared sample was treated with diluted hydrochloric acid (1% v/v) to remove the metallic impurities (if present in sample) and dried at room temperature prior to analysis. The observations of EDS for both samples were summarized and presented as Table 4.7. The EDX spectrum for chemically treated sample (Fig. 4.5) and Table 4.7 clearly demonstrated that the contribution of pure SiO_2 molecule in prepared sample is about 99% and other impurities are under 1% level which are listed as Cobalt (Co), Tungsten (W), Zinc (Zn), Iron (Fe),

Magnesium (Mg), Chromium (Cr)and Lead (Pb). Tungsten (W) contamination in prepared sample was found more active in comparison to other impurities and involved at 0.05-0.86% level. Results also indicated the benefits of acid treatment for sample preparation as it has clearly revealed that percentage of Tungsten impurity has been significantly reduced by adopting this treatment.

Table 4.7 Atomic percentage of elements in nano synthetic quartz sample by EDX study.

Chemical Treatment	Atomic Percentage of Elements in sample									
	Si	O	Al	Co	W	Zn	Fe	Mg	Cr	Pb
Without chemical treatment	18.27	80.55	-.	0.01	**0.86**	-	0.10	0.02	-	0.02
with chemical treatment	31.17	68.35	-	0.04	**0.05**	0.10	0.10	-	0.12	0.07

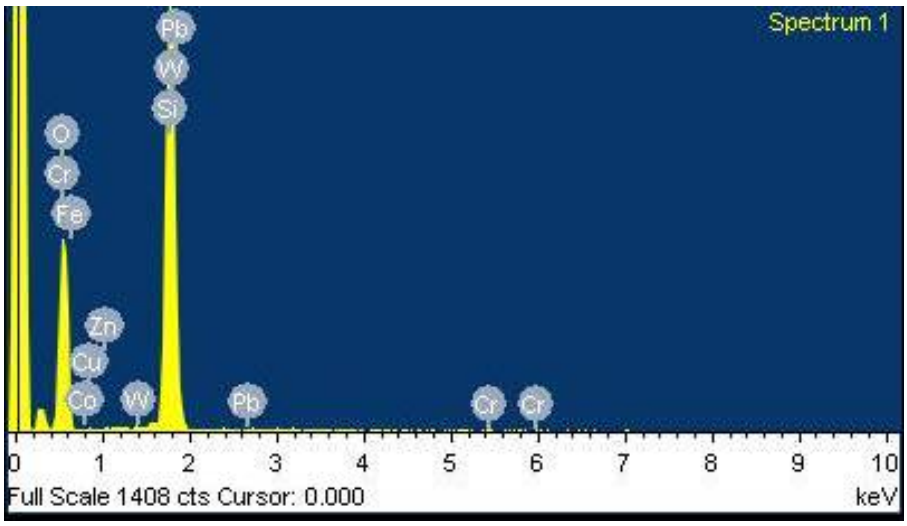

Fig.4.5 EDX image of chemically treated nano synthetic quartz sample.

4.3.6 Fourier Transform Infrared Spectroscopy (FTIR) Study

FTIR spectroscopy is most suitable technique for identification of the functional group (-OH, -CH_3, -COOH etc.) that are either present in minerals, organic or inorganic substance[15]. Several scientists have used this technique for the identification of -OH impurity in natural as well as synthetic quartz material to establish correlation with luminescence emission. Their work revealed that such impurity is related to defects; and act as non-radiative

recombination centre or as a trapping centre, to compete with radiative recombination centres during luminescence processes[16-18]. The EDX spectrum has described the information about the contribution of various impurities present in the nano sized sample. But other impurities like -OH group which could not be resolved by EDX technique and may affect on the structural properties of the sample can further be characterized by FTIR spectroscopy.

The FTIR spectrums were recorded over wavelength from 4000 cm^{-1} to 600 cm^{-1} for the un-annealed nano synthetic quartz sample (Fig.4.6). From these spectra, the significant series of broad absorption peaks are observed between 3200 cm^{-1} to 3600 cm^{-1} which are associated with the contribution of O-H stretching mode of hydroxyl group. The later part of the broad peaks are observed between 900 cm^{-1} to 1100 cm^{-1} which is associated to silicate ion[15]. The growth of O-H stretching mode in the hydroxyl group in the present proposed grains may be responsible to loss of luminescence signals with decrease in the particle size.

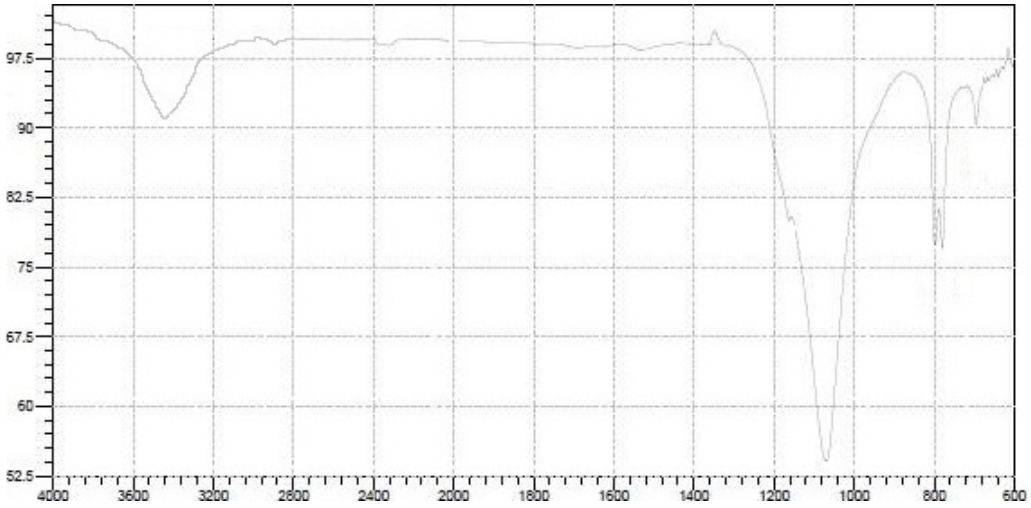

Fig.4.6 FTIR image of prepared nano-sized synthetic quartz sample.

4.3.7 UV-Visible spectroscopy study

A UV-Visible spectrum is a graphical depiction of the absorbed or transmitted light by material as a function of wavelength. Researchers have done a lot of work on the optical absorption behavior of luminescence phosphor. They explained that the defects in the material are responsible for the absorption of light or radiation[19-21]. Absorption spectra have also been used for the measurement of band gap of semiconductors and insulator materials by

researchers[7]. In the present work, due to use of micron sized material as a starting material, it is very necessary to know about defects which are responsible for the absorption of the light and change in band gap of the nano sized sample. In present study, absorption spectra were examined for both types of un-annealed and annealed nano samples followed by different beta doses.

UV spectra of as received samples followed by 2.52Gy and 5.04Gy beta doses have exhibited optical absorption intensity around 0.14 to 1.664a.u. for broad range of peaks from 200-258nm (Fig. 4.7). The positions of these peaks remain identical but notable absorption by 2 to 2.5a.u is 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 beta dose (Fig.4.8). This absorption peak is suggested to be due to the presence of E_1' centres (defects associated with oxygen vacancies) in synthetic quartz samples[22]. Therefore, it can be observed that annealed samples are more optically active in comparison to un-annealed samples.

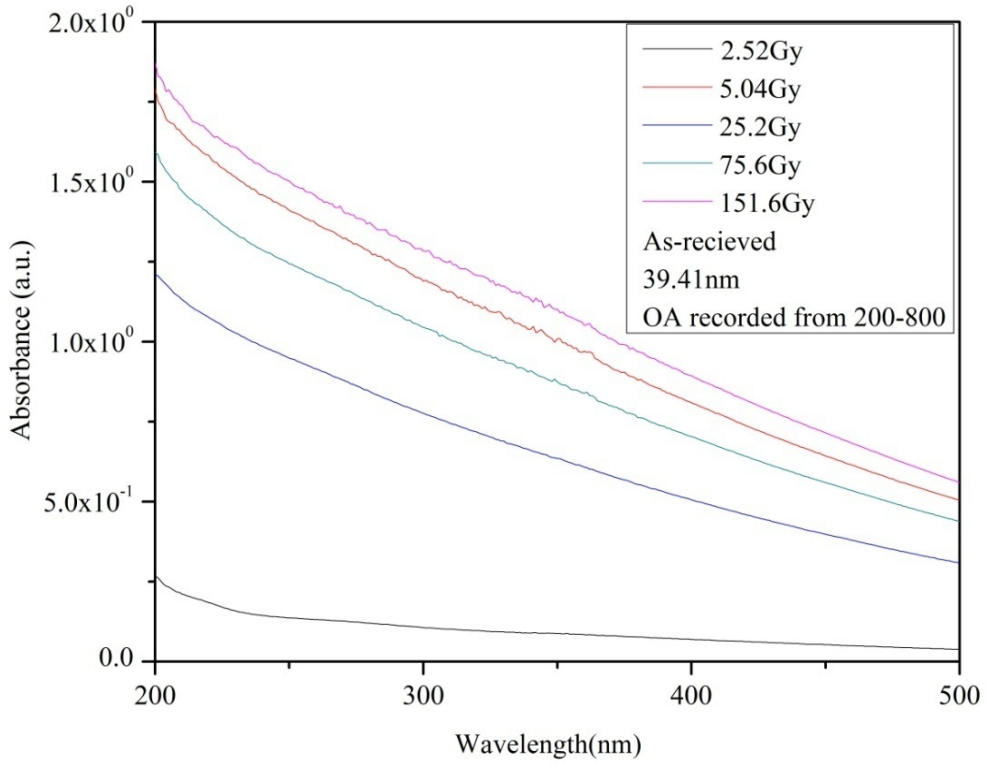

Fig.4.7 UV-Visible spectra of prepared un-annealed nano-sized synthetic quartz sample.

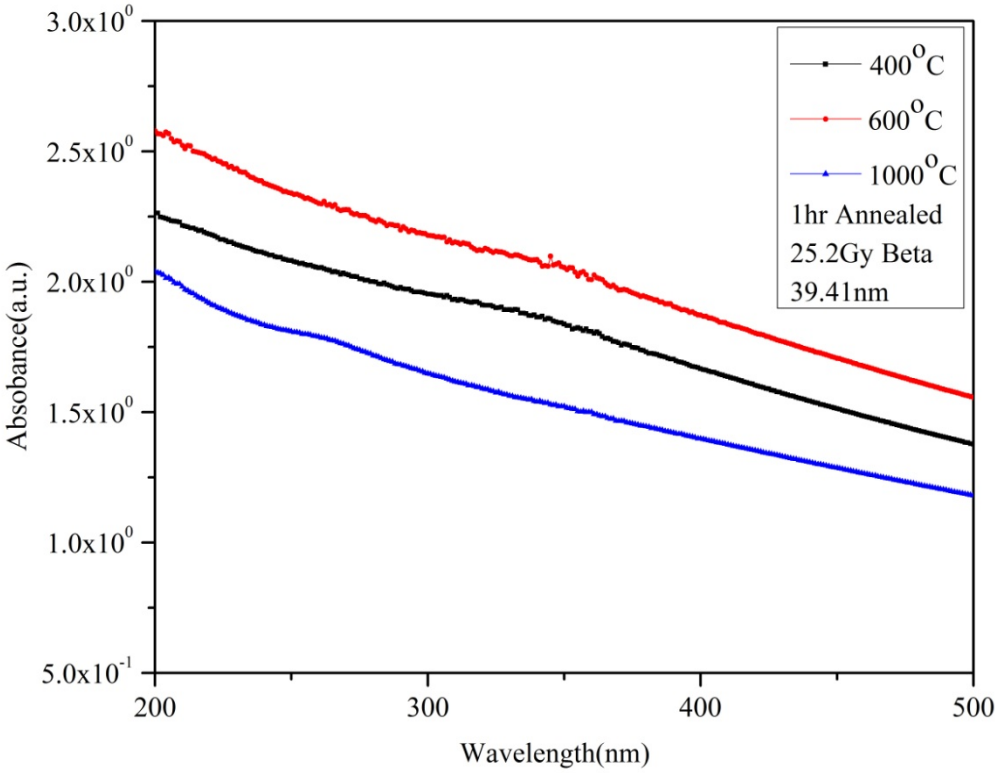

Fig.4.8 UV-Visible spectra of prepared nano-sized synthetic quartz samples annealed at 400°C, 600°C and 1000°C.

4.3.8 Photoluminescence Analysis

PL intensity and emission spectra both contents provide direct information about the surfaces, interfaces and impurity levels of the materials. Researcher used PL emission spectra to detect impurity levels and for the selection of wavelength which will be used as a stimulation wavelength in optically stimulated luminescence measurement[23,24]. Therefore, PL emission spectra of un-annealed nano synthetic quartz sample was recorded and studied for the selection of stimulation wavelength and defects in the material.

The PL emission spectra of nano synthetic quartz sample with excitation wavelength at 254 nm followed for 25.2Gy beta dose are shown in Fig. 4.9. The peaks observed at 371nm, 385nm, 400nm shows the signatures of oxygen vacancy, [AlO_4/Li^+] centre and intrinsic emission respectively whereas the peaks developed at 451nm, 471nm, 482nm, 493nm may stand for intrinsic defect, self-trapped exactions and $[AIO_4]^0$ centre, respectively.[25] PL study has revealed the most suitable wavelength (470nm) as a stimulation wavelength source for OSL process.

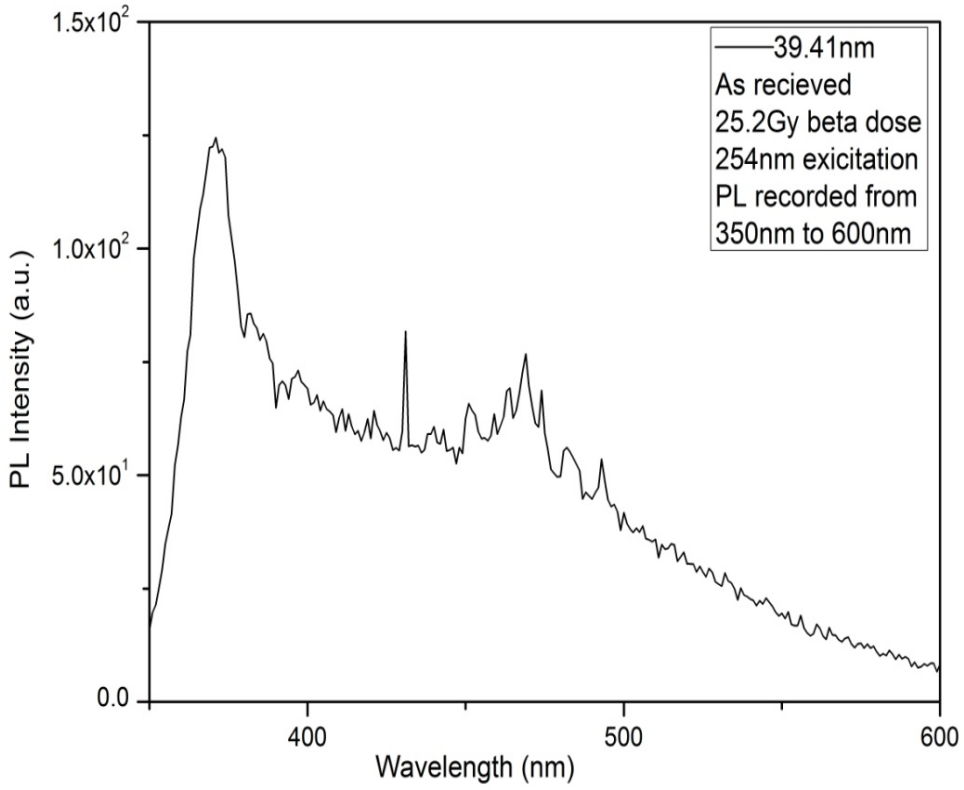

Fig.4.9 PL emission spectra of un-annealed nano synthetic quartz sample.

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