Synopsis of the thesis entitled

OPTICALLY STIMULATED LUMINESCENCE STUDY OF SYNTHETIC QUARTZ AND THEIR APPLICATIONS

To be submitted to

The Maharaja Sayajirao University of Baroda

For the degree of

Doctor of Philosophy
In
Applied Physics

By

Sanskriti Parashar

Under the supervision of

Dr. D. R. Joshi

Applied Physics Department
Faculty of Technology and Engineering
The M. S. University of Baroda
Vadodara- 390 001

Dec 2018

INTRODUCTION

Quartz or Silicon Dioxide (SiO_2), the most common constituent of the earth, is known as α-quartz or natural quartz crystal. It is a brittle, hard, water-resistant and chemically stable material. Due to typical piezoelectric properties of this crystal, it is used for the production of electronic frequency control device as a resonator and filters in electronic circuits. Also, it is widely used as radiation dosimeters and age determination of geological/archaeological samples as a luminescence dating[1,2]. A naturally occurring material, it contains various twins and imperfections which are responsible for degradation of electronic properties of the material. It shows complex output in luminescence dating (Thermoluminescence (TL) or Optically Stimulated Luminescence (OSL)) decay. This is due to origin of the material, internal structure and influence of environmental physical condition to the sample. To avoid these problems, researchers have developed synthetic quartz crystal by hydrothermal technique at laboratory level[1]. Level of impurities, twins or other imperfections and physical condition to the sample can be kept at optimum level by controlling the growth condition of the specimen.

Literature shows, the various physical treatment to the samples like ionizing radiations, optical bleaching, annealing temperature, duration of annealing temperature, heating rates and grain size are responsible for the changes of TL glow curve (intensity and temperature illustration) pattern[3,4]. During TL measurements, the effect of thermal quenching has reduced the TL output due to loss of deep TL traps. The non-destructive optical nature of OSL is a potential advantage over TL, particularly in geological dating and dosimetry. The OSL offers the advantage over TL that the dose dependent OSL signals can be measured several times from the same dosimeter which is not possible in TL. The higher accuracy and reliability is obtained in OSL processes owing to the absence of black body emission[5,6].

The OSL arises from the recombination of charges which have been optically released from electron traps within the crystal. The electron populations in the traps are due to influence of physical treatments to the sample prior to OSL measurement and it is depending upon the magnitude of physical treatments. The optically released charge represents the usual exponential pattern of decay curve over the intensity and time scale[6].

AIM OF THE WORK

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. A. H. Ranjbar et al[7] have recorded the TL glow curves for different micron grain sized clear fused quartz. He has 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 luminescence outcomes are correlated to the sweeping of the centres during grinding process which are responsible to the changes in TL pattern. Further, several workers[8,9] have recorded OSL decay curves at room temperature for single grains of 63-53µm. Prior to 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 critical level. Below critical level of physical conditions, the shape of decay was not in usual exponential nature. Initially, it increases and reaches to maximum OSL followed by usual exponential decay which give rise weaker OSL. The OSL outcomes were corroborated by the ESR studies and also by the TL measurements.

Bhushan and Kohler et al[10,11] reveal that nano size 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. Further, the surface cross-section area per unit volume is increased with decrease in grain size and active/inactive surface defect are responsible for changes in luminescence signals[12,13].

To understand the TL/OSL properties of nano particle sized synthetic quartz material, the present work, is aimed to study the effect of nano particle size followed by physical treatments (annealing temperature and radiation). These studies may suggest novel application of nano synthetic quartz as a radiation dosimeter. The interpretations of the outcomes of the TL/OSL results also been correlated with (i) different characterization of the nano particles such as Particle size analysis, EDS, SEM, TEM, XRD, FTIR etc. and (ii) response of nano particles toward the physical treatments followed by their changes in luminescence properties. The outcomes are resolved by the TL measurements, the components of OSL decay curves and Electron Spin Resonance (ESR) study.

Prior to OSL and TL measurements, as a study of physical structure/characterization of the nano material, the following characterizations have done for the conformation of the nano scale and composition of the material.

[A] EDX Study

Nano-sized synthetic quartz sample is prepared by ball mill process. It may be possible that the contamination or process impurities are present in the material. Therefore, the purity of nano sized samples was checked by EDX technique and was found pure.

[B] Particle Size Analysis

The particle size analysis showed average grains are in 87 nm in range.

[C] SEM Study

The SEM technique confirmed the particle size in nano scale but shapes of the particles are irregular and agglomerated.

[D] TEM Study

A TEM spectrum is showed that the grains of the sample are in nano range (below 100nm).

[E] XRD Study and [F] FTIR Study

The crystalline size of 39.41nm is confirmed by XRD analysis. The FTIR analysis has confirmed the presence of hydroxyl group in the prepared nano sized synthetic quartz samples.

Further, as a response of nano grains towards the physical treatments followed by luminescence study, the following experiments were performed.

[G] Optical Absorption Study for as received sample followed by beta doses

[H] Optical Absorption Study for annealed samples followed by beta doses

Optical absorption spectra were recorded to understand the absorption of light capacity by color centers, which may be available in nano synthetic quartz under the influence of physical conditions. As received 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 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 dose than as received samples.

[I] PL Study for as received sample followed by beta dose

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

[J] TL Study from 25-398^{o}C for as received sample followed by beta doses

[K] TL Study from 25-398^{o}C for annealed samples followed by beta doses

To understand the contribution of the thermally sensitive traps and change in their position under different physical conditions, TL study was performed for as received and different annealed (400°C, 600°C, 1000°C) nano samples followed by beta doses. As received nano material followed by beta exposures 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 disappeared by 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 is sustained in 400^{o}C, 600^{o}C and 1000^{o}C annealed sample of 1hour duration followed by identical exposures. But, 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 as received specimen. However, the strength of 110^{o}C TL peak decreases with rise in annealing temperature to the samples.

[L] OSL Study at 25^{o}C for as received sample followed by beta doses

[M] OSL Study at 25^{o}C for annealed samples followed by beta doses

To observe the contribution of the optically sensitive traps and shape of decay curve under different physical conditions, OSL study at room temperature was performed for as received and different annealed (400°C, 600°C, 1000°C) nano samples followed by beta doses.

The as received samples were exposed to 15.76Gy, 48.03Gy, 81.43Gy, 120.83Gy, 160.23Gy and 199.63Gy 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 samples. 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 are 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 as received sample. The OSL sensitivity under influence of beta doses is weaker in 1000^{o}C annealed sample than lower annealed and as received materials.

[N] TL Study from 25-398^{o}C after OSL at 25^{o}C for as received sample followed by beta doses

[O] TL Study from 25-398^{o}C after OSL at 25^{o}C for annealed samples followed by beta doses

After OSL readout, TL observations are performed because it is necessary to observe that thermally sensitive traps are still contributed in output signals or not and also to develop the correlation between OSL and TL signals. The as received 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.

[P] OSL Study at 160^{o}C for as received sample followed by beta doses

[Q] OSL Study at 160^{o}C for annealed samples followed by beta doses

As received and annealed samples were irradiated by identical beta doses followed by optical stimulation at 160^{o}C for 100second. The as received 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 as received samples.

[R] TL Study from 25-398^{o}C after OSL at 160^{o}C for as received sample followed by beta doses

[S] TL Study from 25-398^{o}C after OSL at 160^{o}C for annealed samples followed by beta doses

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

[T] ESR Study for as received 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 as received and annealed samples followed by beta doses. Either for as received or lower annealed samples show significant involvement of low temperature TL traps which are related to availability of E_1 centers. The losses of luminescence counts may due to diminishing of E_1 centers and growth of new centers which may be correlated to development of higher temperature TL glow peaks in 1000^{o}C annealed material.

The present work is divided into seven chapters. Chapter one titled "Introduction" describes the application of synthetic quartz along with TL, OSL and the aim of the present work. Chapter two deals with the crystallography of quartz in different domain as natural, synthetic as nano and micron size. Experimental methods for characterizations (including TL and OSL) using nano size particle of synthetic quartz are described in Chapter three. Result and discussion about Characterization of Nano-sized Synthetic Quartz are discussed in Chapter four. Chapter five deals with result and discussion of luminescence study (TL, OSL and ESR) of nano synthetic quartz. Chapter six presents conclusions and future plan of work.

References

1 Saha, P., Annamalai, N. & Guha, A. K. Synthetic quartz production and applications. *Transactions of the Indian Ceramic Society* **50**, 129-135 (1991).

2 Preusser, F. *et al.* Quartz as a natural luminescence dosimeter. *Earth-Science Reviews* **97**, 184-214 (2009).

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

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 (1990).

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

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

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).

****

Synopsis Submitted by

Ms. Sanskriti Parashar

Endorsement of the Supervisor:

Synopsis is approved by me

Dr. D. R. Joshi

Head

Dr. B. S. Chakrabarty

Applied Physics Department

Dean

Prof. Arun Pratap

Faculty of Technology and Engineering
The M.S. University of Baroda

❖ PUBLICATIONS & PRESENTATION

- **Sanskriti A Parashar**, Y D Kale, Y H Gandhi, K V R Murthy, D R Joshi; “A Study On Correlation Among Particle Size, UV Absorption And Photoluminescence Of Synthetic Quartz”, International Journal of Luminescence and applications, Vol.6 (1) February, 2016, pages 61-64.
- **S. A. Parashar**, Y. D. Kale, Y. H. Gandhi, D. R.Joshi; “Optical and Photoluminescence studies of synthetic quartz nanoparticles prepared by high energy planetary ball milling technique”, International journal of Luminescence and its application, Vol.5(I), February 2015, pp.69-72.
- **S. A. Parashar**, T. B. Akhani, Y. D. Kale, Y. H. Gandhi, D. R.Joshi, J. D. Baraliya, H. H. Joshi; ”Thermoluminescence Study For Different Grain Sizes Of Annealed Synthetic Quartz Material”, International journal of Luminescence and its application, Vol.2(I), August 2012, pp. 90-91.
- Oral presentation in National Conference on Luminescence and its Applications NCLA-2017 held on 9th-11th January 2017 at IICT, Hyderabad. [Proceedings ISBN No.:978-93-82570-85-1, Paper ID No-1115, Page No.- 115]
- Oral presentation in International Symposium cum workshop on Luminescence Materials ISWLM-2015 held on 18th-20th December-2015 at The M.S. University Baroda, Vadodara.
- Poster presentation in National Seminar on Recent Trends in Experimental Condensed Matter Physics (RTECMP - 2017) held on 21st March 2017 at Saurashtra University, Rajkot. [Abstract book, Page No.- 12]
- Poster presentation in National Conference on Luminescence and its Applications NCLA-2016 held on 18th-20th February 2016 at RTM Nagpur University, Nagpur. [Proceedings ISBN No.:978-93-82570-72-1, Paper ID No-1351, Page No.- 255]
- Poster presentation in 4thInternational Conference on Luminescence and its Applications ICLA-2012 held on 7th-10th February 2012 at IICT, Hyderabad. [Proceedings ISBN No.:81-6717-806-5, Index No. TL-51, Page No.- 357]