2.1 Introduction

Several varieties of natural quartz-like smoky, rose, citrine and amethyst etc. are available on the earth. It is most important silica mineral, occurring in large amounts in igneous, sedimentary and metamorphic rocks. Quartz is a brittle, hard, water-resistant and chemically stable material with twins and other imperfections. Due to typical piezoelectric properties of this crystal, it is used for the production of the electronic frequency control device as a resonator and filters in electronic circuits. It is also widely used as radiation dosimeters and as a luminescence dating age determination of geological/archaeological samples[1,2]. Quartz has many applications in the optical and electrical field due to its structure sensitive property. Natural quartz includes several twins and impurities that are responsible for the degradation of the material's electronic properties and complex production in luminescence dating. To avoid these problems, researchers have developed synthetic quartz crystal by hydrothermal technique at laboratory level[1]. The level of impurities, contaminations, twins or other imperfections and physical condition to the sample can be frozen at the optimum level by controlling the growth condition of the specimen. Therefore, crystallography of quartz in different domain as natural and synthetic is discussed below:

2.2 Structure of Natural and Synthetic Quartz

Quartz and its different polymorphs exist in varied temperature-pressure range along with distinct crystal structure. Tridymite and cristobalite form of quartz exist naturally as minerals in the temperature range 870°C to 1470°C and above 1470°C respectively, both are metastable at ambient temperature. Alpha (α) quartz (natural quartz) exists at low temperature, and on heating beyond 573°C temperature, it transforms into beta (β) quartz. Beta quartz is stable between 573°C to 870°C temperature range. The transition from α-quartz to β-quartz shows small adjustment of atomic positions without any bond rearrangement .This rearrangement of phase change is reversible[3].

Researchers[4,5] observed and explained different phase transformation temperature, which examined with micron-size natural quartz crystal. The findings stated the phase transformation of quartz crystal in the following manner[6]:

α-Quartz $\xrightarrow{@\ 573°\mathrm{C}}$ β-quartz → β-Tridymite $\xrightarrow{@\ 870°\mathrm{C}}$ β-cristobalite $\xrightarrow{@\ 1470°\mathrm{C}}$ liquid Silica

Crystal structure of quartz is constructed by SiO_4 tetrahedral. It is attached by sharing each of their corners with another tetrahedron. It has a compact structure and composed by a hexagonal prism and rhombohedral forms inclined to the c-axis. In a projection perpendicular to the c-axis, alpha quartz depicts larger channels of triad symmetry defined by the position of six trigonal spirals of SiO_4 tetrahedral (Fig.2.1). The trigonal spirals are twist either clockwise or anticlockwise. Therefore it is producing two enantiomorphic forms[2] (Fig.2.2).

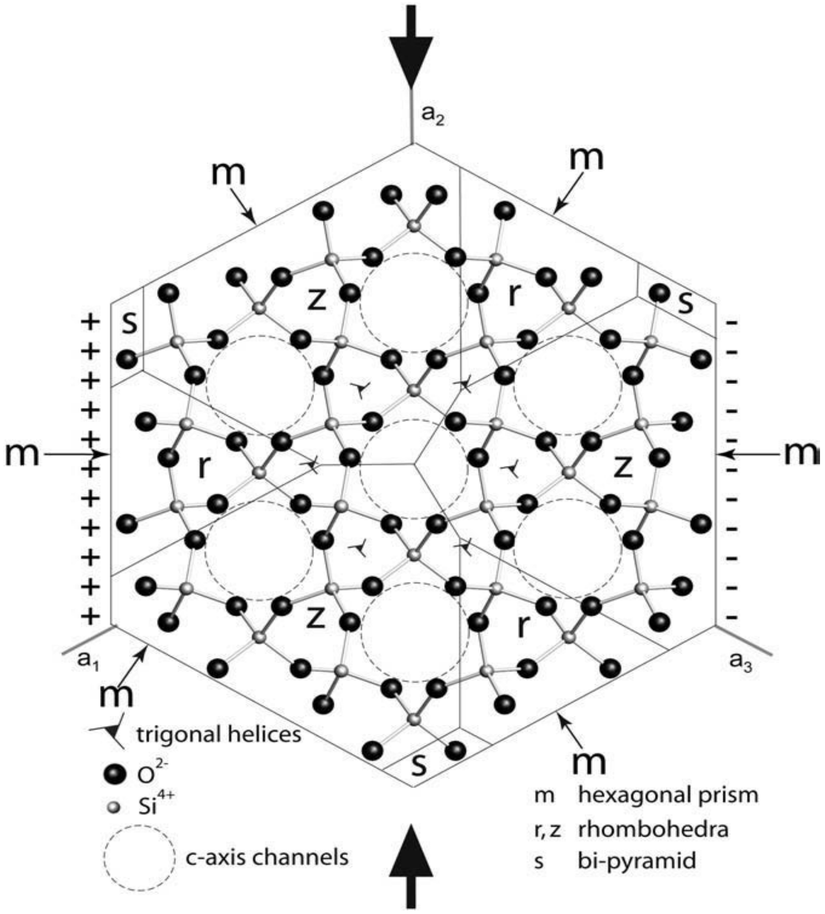

Fig. 2.1 Projection of alpha quartz along with its c-axis displays bigger channels of triad symmetry[2].

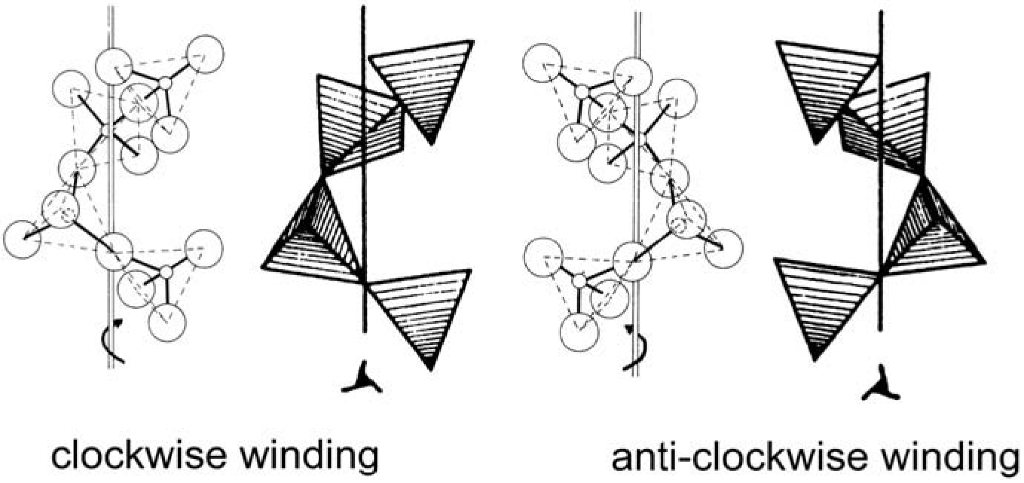

Fig. 2.2 The binding nature of SiO_4 spiral along the trigonal axis of alpha quartz[2].

Alpha quartz crystallises in the form of rhombohedral whereas beta quartz crystallises in the form of hexagonal structure. The oxygen atoms tetrahedrally shared between those of silicon in both ways. In alpha quartz, two of the Si-O bonds create an angle of 66° with the c- axis while another two generate an angle of 44°. Therefore, oxygen occurs in two equivalent pairs. The type of the Si-O bond in SiO_2 defined as being ~40% ionic and ~60% covalent. The rigid structure of the material is attributed by covalent compound, as a result of that, microscopic diffusion of lattice atoms are prevented. Defects like intrinsic and dislocation exist in material, but it becomes a complex structure. Out-of-place lattice atoms tend to place near impurities. Mixed ionic and covalent nature of SiO_2 lattice has resulted by two types of mechanism. One of the ways is damage by radiation means Si-O bond rupture by ionising radiation and another way is direct collision resulting interstitial and vacancy creation. Most of the defects raised due to ionising radiation, appear at pre-existing impurities and imperfections. The trapped electron and hole populations are responsible for optical absorption, luminescence, magnetic and electrical phenomena[3].

Synthetic quartz is prepared in the laboratory by hydrothermal method. It is free from imperfections as compared to natural quartz. But, its polymorphs (alpha, beta, tridymite and cristobalite) are same; occur at the same temperature-pressure condition as in natural quartz. Crystalline quartz structure is formed by SiO_4 tetrahedral, and each of their corners shared with another tetrahedron. In which alpha quartz is mostly lengthened along the c-axis while beta quartz shows compact isomorphic shape. Trigonal structure of alpha synthetic quartz changed into a hexagonal structure known as beta at 573°C temperature, but on cooling, beta instantaneously reverts into alpha synthetic quartz as same as in natural quartz[7].

2.3 Defects in Natural Quartz and Synthetic quartz

The presence of defects in quartz can change its structural, electrical and optical properties. Several factors, such as growth processes, ionising radiation, mechanical stress, change in temperature and the presence of impurities may cause the formation of the defects and predominate to pre-existing defects by other types of defects. All types of quartz (natural and synthetic) contains number of point defects (intrinsic and extrinsic) which are most important for luminescence aspects[2]. They function as an electron and hole centers, which are listed below:

1. Intrinsic defects
    - a. Electron center (with oxygen vacancies)
    - b. Hole center (silicon vacancies)
2. Extrinsic defects
    - a. Electron center (Germanium, Titanium and in general M^{+4})
    - b. Hole center (Aluminium, with iron and in general with M^{+3}, M^{+2} ions, as well as atomic hydrogen)

2.3.1 Intrinsic defects

The intrinsic defects created due to absence of Si and O atom from their crystalline position results in to Silicon and Oxygen vacancies centres.

2.3.1.1 Oxygen vacancy centers

When oxygen atom is removed from perfect alpha quartz with irradiation by ionizing particles, then this type of vacancy centre is reported as neutral O vacancy. It is also known as a diamagnetic centre but E'_1, E'_2 and E'_4 are known as a family of paramagnetic E' centers[2]. The hole which is trapped at neutral O vacancy can design as E'_1 centre. Due to this defect, the resultant unpaired electron shifted towards one of the two Si atoms and the remaining positively charged Si ion transferred into the nearby plane configuration from the vacancy[8]. It was reported that E'$_2$ and E'$_4$ centres also consist of the same O vacancy and related to the presence of H ions. The researcher reported based on ESR data that when the unpaired electron located in either the short bond of the E'$_2$ or the long bond of the E'$_4$, these centres are present[9]. There are number of O excess centres detected in amorphous silica. It was reported that non-bridging oxygen hole centres and proxy radicals are two of O excess centres which was recognized in neutron-irradiated crystalline quartz[2].

2.3.1.2. Silicon vacancy centres

Silicon vacancy contributes to hole trapping by two oxygen ions, and O_2^{-3} center are formed, which can form only on two of four O-O edge of the SiO_4 tetrahedron. Silicon vacancy can also create H_3O_4 and H_4O_4 centre by hosting three or four H ions[2].

2.3.2 Extrinsic defects

During crystal growth, many elements are present in the quartz in the form of impurities, which plays the role of defects. Some new impurity related defects are produced by modification of existing defects due to irradiation. There are mainly two types of impurity defects: first substitutional defect and another is an interstitial defect. Substitutional defects arises due to Al, Ge, Ti, P and Fe elements substituted for Si, and interstitial defects arise when interstitial ions like Li, Na and H can move along the c-axis channels once radiation has freed them[2].

2.3.2.1 Substitutional defect centers

2.3.2.1.1 Al centres

Al is trivalent, and any Al^{3+} which substitutes for Si^{4+} have general tendency to accomplish charge compensation from the presence of an monovalent ion (H^+, Li^+ and Na^+). A positive hole trapped in the vicinity of an Al ion gives another possibility. The resultant centers are known as $[AlO_4/M^+]^0$, $[AlO_4/H^+]^0$ and $[AlO_4]^0$ respectively. If, the charge compensation by an alkali ion (M^+), a hydrogen ion or a trapped hole, among these centres, only $[AlO_4]^0$ is a paramagnetic defect.

From these three-centers, $[AlO_4/M^+]^0$ centers comprise of an Al^{3+} ion in the c-axis channel with an adjacent interstitial alkali ion. The concentration of alkali ions in quartz can be modified by electro-diffusion treatments (sweeping). When this sweeping accomplished in air at room temperature, alkali ions are replaced by H^+ at the Al^{3+} sites. The alkali ions get separated under Temp. > 200K irradiation and are then free to move in the channel along the c-axis. The $[AlO_4/H^+]^0$ consists of an interstitial proton bound to an oxygen ion, i.e. (an OH^- like ion) adjacent to a replacement Al. $[AlO_4]^0$ center comprises of a hole trapped in non-bonding p orbital of an O ion located adjacent to the replacement Al[2].

2.3.2.1.2 Fe centres

Amethyst, citrine, smoky quartz and variety of natural quartz containing iron as Fe centre. It is reported that three paramagnetic centres, named S_1 ($[FeO_4/Li^+]$), S_2 ($[FeO_4/H^+]$), S_3 ($[FeO_4/Na^+]^0$) can also be present in quartz[2].

2.3.2.1.3 Ge centres

At diamagnetic precursor $[GeO_4]^0$, electron trapping formed $[GeO_4]^-$ a paramagnetic centre which is unstable above 20°C and possible decays to the stable $[GeO4/M]^0$centre as a result of arrival by diffusion of charge compensating cation M^+ at Ge site[2].

2.3.2.1.4 Ti centres-

It is also diamagnetic precursor $[TiO_4]^0$ like Ge**.**

2.3.2.1.5 P centres

It is present in rose quartz as P^{5+}**.** After irradiation, paramagnetic $[PO_4]^0$ centres are formed by capturing an electron[2].

2.3.2.2 Interstitial defect centers

Interstitial ions have weak bond with their position. So they can be freed by radiation and can travel along the c-axis channels[2].

2.3.2.2.1 Alkali ions

Monovalent alkali cations integrate along the c-axis channels on full interstitial sites with 4- or 6-fold coordination. Li^+ is most common, but there may be Na^+

and K^+ as well. Such ions are important for charging of substitute trivalent impurities, but they can also be tied to electron trapped at low temperature in SiO_4 complex ($[SiO_4^- /M^+]^0$)[2].

2.3.2.2.2 Hydrogen ions

Presence of Hydrogen ions find in a wide range of defects in quartz. They may have existed since the crystal was formed or may join the crystal much later or may extract at some stage as a result of high-temperature treatments. H^+ ions form H_3O_4 and H_4O_4 by entering at Si vacancy. Because of low-temperature irradiation, both centres can absorb a hole resulting in $[H_3O_4]^0$ and $[H_4O_4]^+$ respectively[2].

Nano materials are attracted considerable attention due to its distinct electronic, optical, chemical and thermal properties[10]. Most of these changes are related to increasing the volume fraction of interfacial regions as the grain size decreases to the range of nanometres[11]. Nanoparticles are expected to have discrete, atomic like energy levels and a spectrum of ultra-narrow transitions that can modify with the size of quantum dot[10]. Chapter one has already described the past literature work of micron synthetic quartz. Though, very interesting and very important from recent applications potential point of view, very less attention was paid to know about the changes in defects and centres at Nano level of synthetic quartz particles. The present work, aims to address these studies in spite of challenges in preparing nano sized synthetic quartz particles. Subsequently, detailed studies of how these changes in defects and centres affect TL and OSL output signals under different physical treatments followed with the specimens are also being considered for developing novel applications using nano sized synthetic quartz.

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