

CHAPTER-2

Quartz, Its Application and Sample

2.1 Introduction to Quartz

Quartz is the second most abundant mineral in the world, after feldspar¹ and its unique properties make it one of the most valuable natural resources. It is also abundant in all parts of the world. Found at all temperatures. It is most igneous, metamorphic, and sedimentary rocks. It is highly resistant to mechanical and chemical climates. This stabilization makes it a major mineral for mountain peaks as well as the main sea, rivers, and desert sands. Quartz is ubiquitous, abundant and durable. Quartz is a solid, crystalline mineral composed of silicon and oxygen atoms. Atoms are connected to a continuous structure of SiO_4 silicon-oxygen tetrahedral, in which each oxygen is distributed between two tetrahedral, providing a general chemical formula of SiO_2 . Inert chemical contact with many substances. It has electrical properties and heat resistance which makes it important for electrical products. Its splendor, color, and variety make it useful for gemstones and for glassmaking.

Quartz exists in two forms, α -quartz and high-temperature β -quartz, both of which are chiral. The conversion from α -quartz to β -quartz occurs abruptly at 573°C (846°K ; $1,063^\circ\text{F}$). Since the change is accompanied by a significant change in volume, it can easily crack cracks or stones passing through this temperature range. There are many types of quartz, most of which are gemstones. From ancient times the types of quartz have been the most widely used minerals in the manufacture of jewelry and solid stone carvings, especially in Eurasia. Quartz is a mineral that defines a value of 7 on the Mohs hardness scale, the first measurement method for obtaining object weight in abrasions.

2.2 Crystal habit and structure

Quartz belongs to the trigonal crystal system. The perfect shape of a crystal is a six-sided bowl that ends with six-sided pyramids at each end. In nature quartz crystals are often fused (with right and left quartz crystals), distorted, or separated by adjacent quartz crystals or other minerals to show only part of this type, or to have a completely crystalline crystal surface and appear larger.²⁻³ Well-formed crystals usually forming like a drum (a layer of crystalline crystals), those quartz geodes are excellent examples.⁴ One finishing tower exists. However, double-coated crystals occur when they grow freely without attachment, for example, inside gypsum.⁵

Alpha-quartz grows in the trigonal crystal system, the space group P3121 or P3221 depending on the severity. Alpha-quartz belongs to the hexagonal system, the space group P6222 and P6422, respectively.⁶ These space groups are really chiral (each of which is a pair of 11 pairs with enantiomorphism). Both α -quartz and β -quartz are examples of chiral crystal structures composed of arch building blocks (SiO_4 tetrahedral in the present state). The transition between α -quartz and β -quartz involves only a small tetrahedral rotation in relation to each other, without a change in the way they are connected.³

Crystal formation of two types of quartz namely α -quartz and β -quartz is shown in Figure 2.1

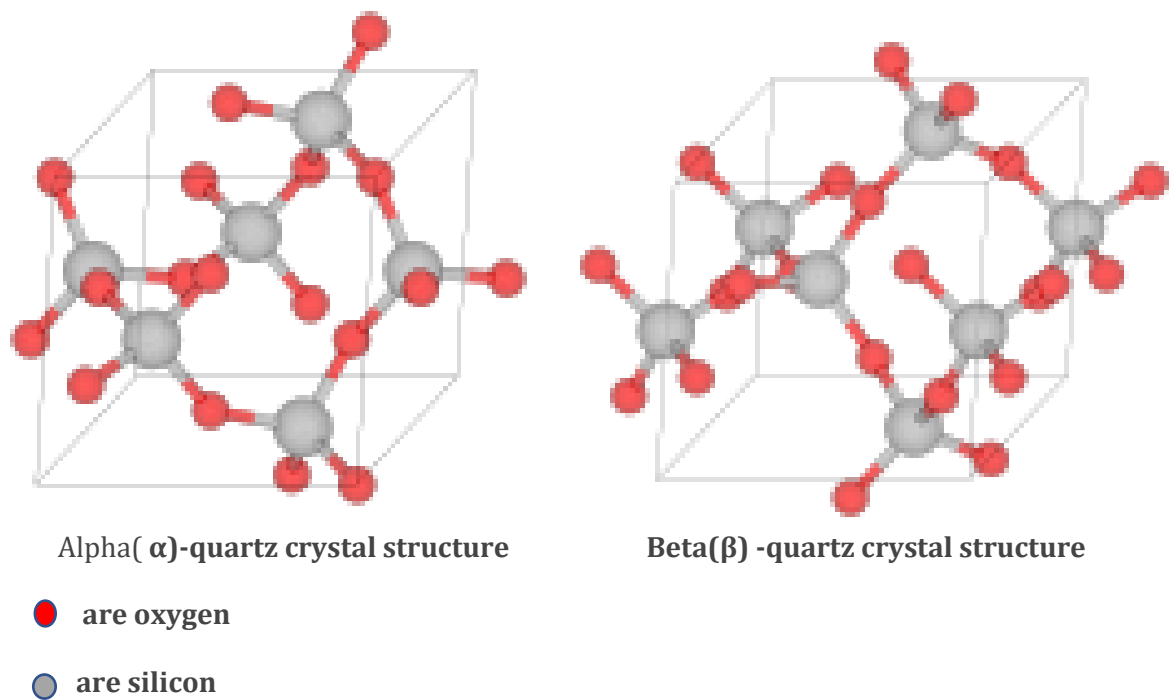


Fig 2.1 Crystal Structure of α -quartz and β -quartz

2.3 Types of Quartz on the basis of microstructure

Although many of the varietal names historically arose from the color of the mineral, current scientific naming schemes refer primarily to the microstructure of the mineral. Color is a secondary identifier for the cryptocrystalline minerals, although it is a primary identifier for the macrocrystalline varieties.⁷

Table-2.1 Various types of Quartz

Major varieties of quartz		
Type	Color & Description	Transparency
Herkimer diamond	Colorless	Transparent
Rock crystal	Colorless	Transparent
Amethyst	Purple to violet colored quartz	Transparent
Citrine	Yellow quartz ranging to reddish orange or brown (Madera quartz), and occasionally greenish yellow	Transparent
Ametrine	A mix of amethyst and citrine with hues of purple/violet and yellow or orange/brown	Transparent
Rose quartz	Pink, may display diasterism	Transparent
Chalcedony	Fibrous, variously translucent, cryptocrystalline quartz occurring in many varieties. The term is often used for white, cloudy, or lightly colored material intergrown with moganite. Otherwise more specific names are used.	
Carnelian	Reddish orange chalcedony	Translucent
Aventurine	Quartz with tiny aligned inclusions (usually mica) that shimmer with aventurescence	Translucent to opaque
Agate	Multi-colored, curved or concentric banded chalcedony (cf. Onyx)	Semi-translucent to translucent
Onyx	Multi-colored, straight banded chalcedony or chert (cf. Agate)	Semi-translucent to opaque

Jasper	Opaque cryptocrystalline quartz, typically red to brown but often used for other colors	Opaque
Milky quartz	White, may display diasterism	Translucent to opaque
Smoky quartz	Light to dark gray, sometimes with a brownish hue	Translucent to opaque
Tiger's eye	Fibrous gold, red-brown or bluish colored chalcedony, exhibiting chatoyancy.	
Prasiolite	Mint green	Transparent
Rutilated quartz	Contains acicular (needle-like) inclusions of rutile	
Dumortierite quartz	Contains large amounts of blue dumortierite crystals	Translucent

2.4 Various use of Quartz⁸

(a) In manufacturing of glass

Geological processes involve sand, which sometimes consists of about 100% quartz grains. These deposits have been identified and produced as sources of high-quality silica sand. These sands are used in the glass industry. Quartz sand is used in the manufacture of glass, flat plate, special glass and fiberglass.

(b) Quartz as Abrasive

The high hardness of quartz, on a scale of seven Mohs, makes it harder than many other natural materials. So that's a pretty good thing. Quartz sand and fine-grained silica sand are used to blast sand, cleaners, grinding media, and grit for sand and sawing.

(c) Quartz as Foundry Sand

Quartz has a property to offer high resistant to chemicals and heat. It is therefore often used as low-grade sand. With a soluble temperature higher than most metals, it can be used for molds and grains for general base work. Stubborn bricks are usually made of quartz sand because of their high resistance to heat. Quartz sand is used as a metal smelter.

(d) Use in the Petroleum Industry

Quartz sand has high resistance to crushing. In the petroleum industry, sand slurries are forced into oil and gas sources under very high pressure in a process known as hydraulic fracturing. This high pressure breaks up the rocks in the lake, and the sandy slurry seeps where it cracks. Long-lasting sand grains hold open cracks after pressure is released. This open cracking facilitates the entry of natural gas into the water hole.

(e) Use of Alternative Quartz Sand

Quartz sand is used as a filler for rubber, paint, and putty. Used and refined quartz grains, carefully used as a media filter and roof granules. Quartz sands are used for gravity in the railway and mining industry. These soils are also used for recreation at golf courses, volleyball stadiums, baseball stadiums, children's sandboxes and beaches

(f) Other Use of Quartz crystals

One of the marvels of quartz is its ability to vibrate crystals in a straight line. These frequencies are so accurate that quartz crystals can be used to make highly accurate timing tools and equipment that can transmit radio and television signals with precise and stable frequencies.

The small devices used for these purposes are known as "crystal oscillators." The first crystal oscillators were developed in the 1920's, and just two decades later, tens of millions of them were needed each year to bring the military into World War II. Today, billions of quartz crystals are used to make clocks, clocks, radios, televisions, electronic games, computers, cell phones, electric meters, and GPS devices.

Various methods have been used for optical-grade quartz crystals. They are used to make special lenses, windows and filters for lasers, microscopes, telescopes, electronic sensors, and scientific instruments. Sea sand equipment has now become one of the most advanced electronic devices in the world.

2.5 Quartz Defects

The luminescence characteristics of quartz impairment have been the subject of a large number of studies aimed at understanding the complex mechanisms that regulate the emission of various luminescence and their modification as a result of radiation and heat treatment.⁹⁻¹⁰ Many defects, both internal and related impurities, are known to

exist or are produced by quartz, as identified by various observations; but so far, the role of this failure in producing luminescence emissions is still being debated. Although a number of studies have been performed on the formation of defects in quartz defects, particularly with ESR¹¹ measurements, only the correlation between error and luminescence extraction has been excluded. Most defects are known to exist in both crystalline (quartz) and the amorphous (silica) types of SiO₂, but the luminous properties of quartz and silica are very different.¹² Quartz, especially the so-called Al centers associated with extraction capacity¹³⁻¹⁴. Other internal or related impurities have been suggested as a mechanism for luminescence extraction in quartz, while only a handful of institutional recommendations are available in the scientific literature to date. It will be recalled that it is often the case that traps and recombination centers are closely related to the environment and some OSL and TL are proposed to be of this type.¹⁵⁻¹⁶ Two major types of quartz defects are reported to be related to its light properties: oxygen spaces, the most common internal defects, and Al centers, the universal type of pollution center. In addition to these defects, other pollutants, such as Ti, Fe, and Ge ions, arise from many defects, and Si spaces are known to exist as allies with oxygen gaps; they provide the origin in the H₂O₄ environments, where the availability of H⁺ ions compensate for the missing Si⁴⁺ charges.

2.5.1 Oxygen Vacancies

The simplest type of O-space is a diamagnetic center that arises from the removal of an O atom from a-quartz is a complete alternative, leaving a direct bond between Si atoms¹⁷. This “neutral O-space” is often referred to as the precursor of the paramagnetic E1' center, which can be defined as a hole stuck in the neutral O-field. To the setting of a nearby aircraft (Figure 2.2)¹⁸ is often regarded as the most likely precursor to E1'; however, this relationship is controversial and E1's predecessor is yet to be identified. Outside the E1 center, E2' and E3' are known to be present in quartz as E1 modification, related to the presence of H ions¹⁹. Another group of institutions with the disease is E". They are very similar to E-centers, where the number of primes indicates how many unpaid electrons the facility has. Specifically, E1", E2", and E3" were reported, indicated by its slightly different ESR symbol. All are extinguished by burning quartz at a temperature of 50°C -100°C.

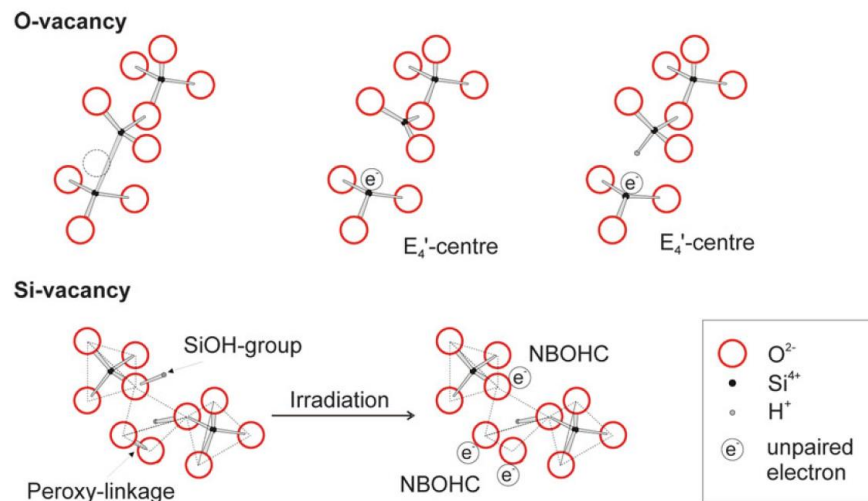
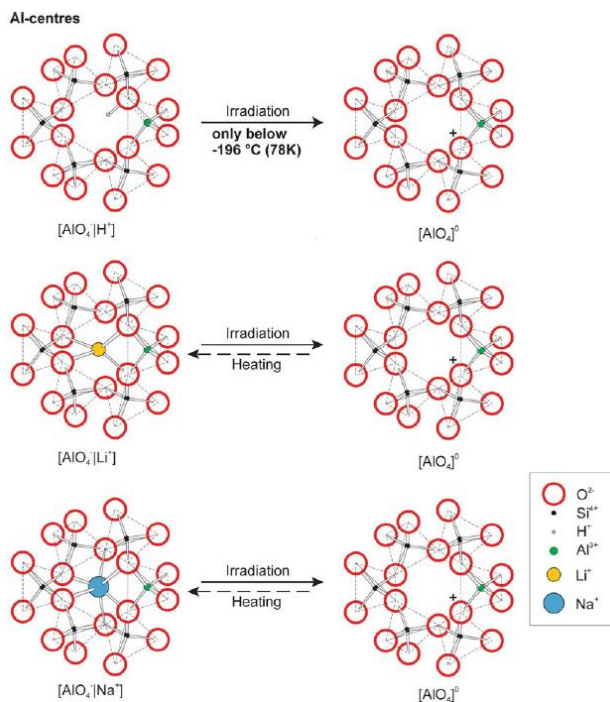


Fig. 2.2 Intrinsic defect centers in quartz⁹

2.5.2 Al Centers

Al^{3+} ion is the main ubiquitous impurity to which many defects are associated. It is present as a substitutional ion for Si^{4+} and is charge compensated by an alkali ion (M^+) or by an H^+ ion, giving rise to $[\text{AlO}_4/\text{M}^+]^0$, $[\text{AlO}_4/\text{H}^+]^0$, respectively. When neither M^+ nor H^+ is present near a substitutional Al^{3+} ion, this latter can be charge compensated by a positive hole, giving rise to the $[\text{AlO}_4]^0$ center (Halliburton et al. 1981). The three kinds of Al centers and their interactions are shown in Fig 2.3

Fig. 2.3 Al centers in quartz⁹



2.6 A Need for Synthetic Quartz Crystals

During the 1900's the demand for high-quality quartz crystals became so rapid that mining operations around the world failed to provide them with adequate value. Fortunately, this need was met during World War II, and the military and the private

sector began to work on ways to grow quartz crystals that were made to meet the special needs of optical and electronic use.

Today, many quartz crystals used in electronic components and optical tools are grown in research facilities instead of in production at mines. Most laboratories grow their crystals using methods that are based on the geological process of hydrothermal activity. Synthetic crystals are grown at high temperatures from hot water rich in dissolved silica. These manufactured crystals can be grown in shapes, sizes and colors to suit the needs of production processes. The cost of growing quartz crystals is competitive with mining, and the only limitation in producing the availability of crystal growth equipment.

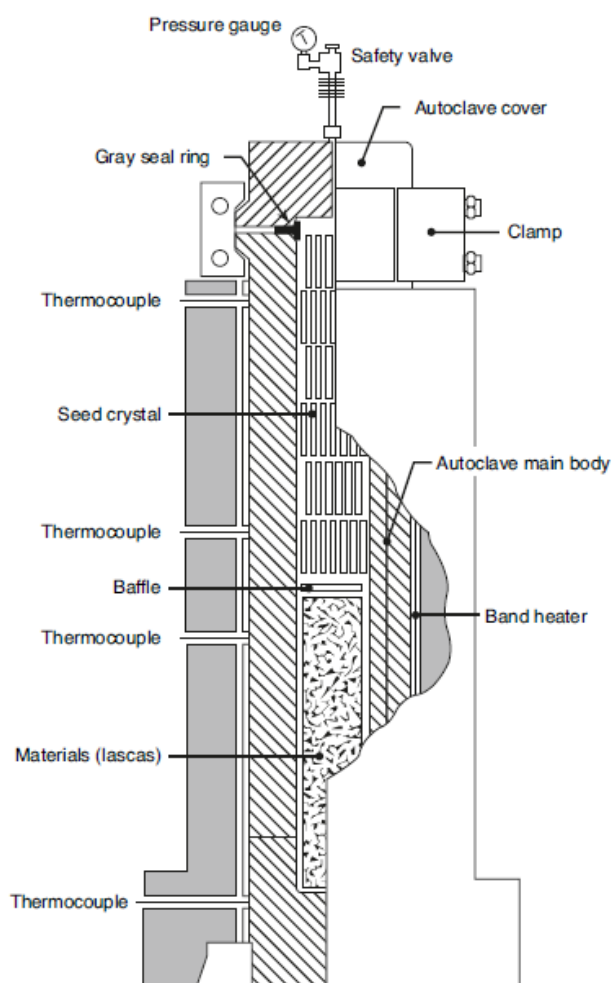
2.7 Preparation of Synthetic Quartz (SQ)

Beginning in 1958, the production of synthetic quartz began at the commercial level. The electronic components that make up the industry have begun to use more laboratory-grown crystals compared to natural quartz since 1971. Central Glass and the Ceramic Research Institute (CGCRI) developed high-tech growth technology in 1972 and successfully demonstrated low-level trading in 1989. The Growth process of Synthetic Quartz single crystals at CGCRI

This process involves following steps

- Nutrient quartz (small crystalline quartz chips) dissolves in aqueous alkaline medium
- Allow them to grow on single crystal seed rods or plates
- This process of dissolution of nutrient quartz and growth on seed rods must take place at high temperature (at about 355°C) and pressure (at about 900 bar), hence the nutrient quartz, the aqueous alkaline solvent medium and seed rods have to be confined in a high-pressure autoclave.
- An autoclave is a vertical cylinder partitioned by a baffle plate with holes into two compartments. Single crystal seed rods and plates are placed in the upper compartment (growth zone) and materials (small pure polycrystalline quartz chips) are placed in perforated basket in the lower compartment (dissolution zone). Around seed rods/plates single crystal synthetic quartz develops. Internal free space of autoclave which is about 75 percent is filled up by pouring it with a 0.5M solution of sodium carbonate/hydroxide with 0.05M dopant level lithium nitrite (Table-2.2).

- The autoclave is then sealed properly to withstand high pressure (about 700-900 bar) that would subsequently be generated and heat is supplied by means of electrical heating elements in such a way that a temperature difference in the range of 5°C to 15°C can be maintained between upper and lower compartment.
- Temperature of the upper growth zone always being lower than the temperature of the lower dissolution zone.
- When the desired temperature and pressure attained, the nutrient polycrystalline quartz chips get dissolved in the aqueous alkaline medium as



Schematic depiction of Synthetic Quartz Growth¹

Fig. 2.4 Synthetic Quartz Growth

- silica and are transported to the cooler growth zone where the single crystal quartz seed rods and plates are located. Here silica-bearing aqueous alkaline medium becomes supersaturated because of lower temperature and silica precipitates out of the solution on to single quartz seed surface.
- In the lower nutrient zone, the cool solution sinks, is heated up there, and again takes up polycrystalline quartz in solution; the supersaturated solution is again transported to the upper cooler growth zone and the whole cycle is repeated continuously. Thus, the synthetic quartz single crystals are gradually built up slowly on the seed rods and plates, and to attain the proper size of the crystals the process has to be continued for typically about 35-45 days. Any attempt to hasten the process by unduly increasing the temperature difference, temperature Or pressure will result in growth of crystals which is not suitable for the electronic industry.²

Table-2.2 Demonstration run for growing synthetic quartz at C.G.C.R.I

1. Run Particulars		
Duration:35 days (in 1989)		
Growth temperature:356 °C		
Temperature difference:9 °C		
Pressure:760 Kg.cm ⁻²		
Solvent:0.5 M Na ₂ CO ₃ +0.05 M LiNO ₂		
Number and Size ranges of single crystal quartz seeds placed inside autoclave:		
Rods (Y- bar) in the size range:		
110-210 mm along Y.....523 nos.		
Z-plates (in X-Y plane) in the size range:		
length 180-205 mm, breadth 45-50 mm.....4 nos		
Run conducted at about 75% of full capacity		
2. Total yield: 39.0 kg		
Crystal perfection	By weight	Yield By percent
a) Flawless		91
(i) Y-bar crystals	35. 5	95
(ii) Z-plate crystals	1.5	4
(b) Flawed	2	5

2.8 Quality rating of synthetic quartz

Errors or impurities can be found in synthetic quartz depending on the growth rate of the crystal, additives, used materials and other materials. Alpha value and temperature range are important indicators of synthetic quartz affected by growth rate. Alpha value rises due to the high growth rate causing variability in normal temperature signals.

The quality of synthetic quartz crystal on its first stage was indicated by the value of Q (Power stored in cycle / Power lost per cycle).

Using a wide range of modern methods and strict quality controls, high quality quartz is produced for quartz crystal products such as crystal unit, crystal filters, SAW devices, optical filters and more

References:

1. Anderson, Robert S.; Anderson, Suzanne P. (2010). *Geomorphology: The Mechanics and Chemistry of Landscapes*. Cambridge University Press. p. 187. ISBN 978-1-139-78870-0.
2. Hurlbut, Cornelius S.; Klein, Cornelis (1985). *Manual of Mineralogy* (20 ed.). ISBN 0-471-80580-7.
3. Nesse, William D. (2000). *Introduction to mineralogy*. New York: Oxford University Press. p. 205. ISBN 9780195106916.
4. Sinkankas, John (1964). *Mineralogy for amateurs*. Princeton, N.J.: Van Nostrand. pp. 443–447. ISBN 0442276249.
5. Tarr, W. A (1929). "Doubly terminated quartz crystals occurring in gypsum". *American Mineralogist*. 14 (1): 19–25. Retrieved 7 April 2021.
6. *Crystal Data, Determinative Tables*, ACA Monograph No. 5, American Crystallographic Association, 1963
7. "Quartz Gemstone and Jewelry Information: Natural Quartz – GemSelect". *www.gemselect.com*. Archived from the original on 29 August 2017. Retrieved 29 August 2017.
8. <https://geology.com/minerals/quartz.shtml#:~:text=Quartz%20is%20a%20chemical%20compound,Transparent%20%22rock%20crystal%22%20quartz>.
9. Preusser, F., Chithambo, M. L., Go tte, T., Martini, M., Ramseyer, K., Sendezera, E. J., Susino, G. J., and Wintle, A. G., 2009. Quartz as a natural luminescence dosimeter. *Earth Science Reviews*, 97, 184–214.
10. Lieb, K. P., and Keinonen, J., 2006. Luminescence of ion-irradiated alpha quartz. *Contemporary Physics*, 47, 305–331
11. Weil, J. A., 2000. A demi-century of magnetic defects in a-quartz. In Pacchioni, G., Skuja, L., and Griscom, D. L. (eds.), *Defects in SiO2 and Related Dielectrics: Science and Technology*. Amsterdam: Kluwer, pp. 197–212.
12. Stevens Kalceff, M. A., and Phillips, M. R., 1995. Cathodoluminescence micro characterization of the defect structure of quartz. *Physical Review B*, 52, 3122–3134.
13. Halliburton, L. E., Koumvakalis, N., Markes, M. E., and Martin, J. J., 1981. Radiation effects in crystalline SiO2: the role of aluminum. *Journal of Applied Physics*, 52, 3565–3574.

14. Martini, M., Fasoli, M., Galli, A., Villa, I., and Guibert, P., 2012a. Radioluminescence of synthetic quartz related to alkali ions. *Journal of Luminescence*, 132, 1030–1036.
15. Itoh, N., Stoneham, D., and Stoneham, A. M., 2002. Ionic and electronic processes in quartz: mechanisms of thermoluminescence and optically stimulated luminescence. *Journal of Applied Physics*, 92, 5036–5044.
16. Martini, M., Fasoli, M., and Galli, A., 2009. Quartz OSL emission spectra and role of [AlO₄] recombination centers. *Radiation Measurements*, 44, 458–461.
17. Feigl, F. J., Fowler, W. B., and Yip, K. L., 1974. Oxygen vacancy model for E'1 center in SiO₂. *Solid State Communications*, 14, 225–229.
18. Rudra, J. K., and Fowler, W. B., 1987. Oxygen vacancy and the E1' center in crystalline SiO₂. *Physical Review B*, 35, 8223–8230.
19. Fowler, W. B., Rudra, J. K., Edwards, A. H., and Feigl, F. J., 1988. Theory of oxygen vacancy defects in silicon dioxide. In Devine, R. A. B. (ed.), *The Physics and Technology of Amorphous SiO₂*. New York: Plenum Press, pp. 107–112.
20. Bossoli, R. B., Jani, M. G., and Halliburton, L. E., 1982. Radiation-induced E' centers in crystalline SiO₂. *Solid State Communications*, 44, 213–217.
21. https://www.ndk.com/catalog/AN-SQC_GG_e.pdf
22. P Saha, Annamalai and A.K.Guha, "Synthetic Quartz production and Applications", *Transaction of Indian Ceramic Society*, vol-50(5), Sept-Oct, pp129-135, 1991