

Fourier transform infrared spectroscopic estimation of crystallinity in SiO₂ based rocks

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Abstract. We present here optical properties and crystallinity index of quartz (SiO₂) in natural rocks samples from the Mikir and Khasi hills, Assam, India. Infrared spectroscopy has been used to study the structure of quartz in rock samples and estimate the mining quality of quartz mineral, which is substantiated by calculating the crystallinity index. Systematic investigations of structure have been carried out in between 10 μm (1000 cm⁻¹) and 20 μm (500 cm⁻¹) bands of silicates. Investigation is based on the assignment of infrared bands to certain structural groups of SiO₄ tetrahedra. The crystallinity of samples has been ascertained by comparing the ratio of intensity of the characteristic peak at 778 and 695 cm⁻¹ with the corresponding ratio for a standard sample. The crystallinity parameter is calculated by using a standard procedure which can be used to estimate the distribution of quartz in various rocks for mining purpose. The infrared spectroscopic investigation is found to be an ideal tool for structure elucidation and for estimating quartz crystallinity of the natural samples.

Keywords. Quartz; crystallinity; infrared spectroscopy; structure elucidation.

1. Introduction

Mining and industrial areas of research can benefit from a geological understanding of quality of mineral processing and properties of minerals. SiO₂, in its various crystalline and amorphous forms, has an extremely wide spectrum on industrial applications. In glass ceramics, ceramics are produced by the controlled crystallization (Beall 1992). In nature, mineral represents the unique pairing of a composition and an ordered internal structure. An additional characteristic is the degrees of crystallinity (e.g. compare quartz crystal to chert/flint to glass) of a material. Quartz is one of the most abundant minerals found in the earth's crust (12% of its weight). It is a major component of numerous igneous and sedimentary rocks and is present in impure state in many siliceous rocks. Crystallinity of quartz is found to be very useful in determining the colour alteration in bedded cherts, as there is a relationship between quartz crystallinity index, grain size of quartz and conodont colour alteration index (Teji *et al* 2002). It has been known that vitreous silica forms as a result of natural phenomenon like lightning strike at the quartz sand or sand stones. Such a fused glass is called fulgurites (Saikia *et al* 2008). Natural fused quartz can also be produced by a combination of temperature and pressure re-

sulting from meteorite impact. Cristobalite and tridymite are the other most common forms of which are commonly known as crystalline silica. Among the most violently alkali-reactive rocks are sand/siltstone, mylonite, acid volcanic rocks, and other rock types containing quartz grains, <60 μm (Heaney *et al* 1994). The extensive natural occurrence of quartz and the wide uses of the materials that contain quartz are directly related to potential occupational exposures to quartz for workers in many industries (e.g. mining, farming, and construction) and occupations. During the 1980s, studies were conducted that suggested that crystalline silica also was a carcinogen. Potentially, exposure to crystalline silica can occur during mining and quarrying, during stone cutting and construction, in foundries and in numerous other activities, including sanding, sandblasting, polishing and grinding. Silicosis is the oldest and most well known disease attributed to inhaling crystalline silica and there is a correlation between crystallinity index and fibrogenicity (Aitree Williams and Sprogis 1982). The X-ray diffraction full width at half maximum (FWHM) of (212) line for α-quartz diffraction line in a sample can then be used to directly assess crystallinity index for the α-quartz. This method greatly enhances the practicability of determining α-quartz crystallinity on individual respirable dust micro samples collected by personal sampling. It is likely that the crystallinity index will prove to be a useful measure of the specific toxicity of α-quartz and, hence, find in-

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corporation into the risk assessment for α -quartz exposure (Aintree-Williams and Clapp 2002).

Quantitative determination of quartz, by infrared spectrophotometry, in dust, soil, other silicates and powdered coal was reported by several workers (Heaney *et al* 1994). Fourier transform infrared spectroscopy provides a potentially rapid method of relatively non-destructive analysis which can be used to establish a database on the crystallinity and trace mineral components of rocks (Parthasarathy *et al* 2001, 2003). Silica polymorphs and their trace mineral components have been recognized using infrared techniques (Rice *et al* 1995). At high temperature and pressure, silica polymorphs pass through a slow reconstructive recrystallization, during which existing Si–O bonds are broken and new bonds are made to allow atoms to move to appropriate positions in the more stable polymorph (Parthasarathy *et al* 2007). Any significant change in the crystallinity can be attributed to the geological conditions of formations and mechanical treatment such as grinding (Murata and Norman 1976). In the present work, we address the infrared technique for estimation of crystallinity of some quartz bearing rocks.

2. Rock formation of study region

Eight selected quartz rock samples were collected from various quarries of Mikir and Khasi hills of north-eastern region of India. Granite and granitic gneisses are found all over the Meghalaya plateau and in the Karbi plateau of Assam. The geneses are associated with garnet–quartzite with or without sillimanite in Khasi hills. The sillimanite bearing rocks of quartz–feldspathic genesis of Archean age are also found in Mikir hills. One of the best sillimanite deposits of the world is found in the Sonapahar region of West Khasi hills. These sillimanite deposits occur in association with corundum, within the quartz–sillimanite schist which forms a broad band that can be traced discontinuously over the area. Quartz is found as pegmatite veins in several localities of Khasi hills (Ramakrishnan and Vaidhyanadhan 2008).

3. Experimental

A part of the sample was crushed into fine powder for analysis, by using agate mortar. We tried to minimize the grinding time to avoid the deformation of the crystal structure and the ion exchange. The powdered samples (0.25 g) were put into platinum crucibles and HNO₃ (conc.), HCl, H₂O₂ and HF were added in the proportion of 5 : 2 : 1 : 2 ml. Crucibles were heated on hot plate and the solution evaporated to near dryness. After that, 2 ml HF were added few times until precipitate of SiO₂ was eliminated as SiF₄ vapours. After cooling down to room temperature, a mixture of HCl (conc.) and redistilled water

at a ratio 2 : 5 ml was added, the solution transferred in 50 ml volumetric flasks and filled up with redistilled water.

Then 0.5 g of powdered sample was put in a glass beaker and a mixture of redistilled water and HCl (conc.) in a ratio 15 : 20 ml was added and the solution evaporated to near dryness. The residue was dissolved with 10 ml 1% tin, and SiO₂ precipitated and coagulated. Precipitate was filtered and washed with HCl solution in a ratio of 5 : 95 ml. Filter paper and residue were transferred into a platinum crucible and heated at 1000°C for 10 min. Crucible was weighed and the content of SiO₂ calculated.

The powdered sample was homogenized in spectrophotometric grade KBr (1 : 20) in an agate mortar and was pressed with 3 mm pellets using a hand press. The infrared spectrum was acquired using Perkin-Elmer system 2000 FTIR spectrophotometer with helium–neon laser as the source reference, at a resolution of 4 cm⁻¹. The spectra were taken in transmission mode in the region 400–4000 cm⁻¹. The room temperature was 30°C during the experiment.

4. Results and discussion

The crystallinity of quartz is recognized as an indicator of crystalline form of other minerals associated with it. Since quartz is crystallized after all minerals associated with it get crystallized, therefore, when crystallinity of quartz is maximum, we can expect that the associated minerals are in well crystalline form. The maximum value of crystallinity indicates the minerals are in ordered form and the minimum value of it is taken as disordered form. Therefore, it is important to find the crystallinity of quartz rather than the other associated minerals.

Figure 1 shows the infrared spectra of the quartz-rich samples from Assam, in the frequency range 500–2000 cm⁻¹. The mid infrared spectra of silicate in between the range 1200–400 cm⁻¹ are classified into four characteristic bands around 1000, 780, 695 and 450 cm⁻¹ with reference to the standard quartz spectra. Among these four characteristic peak regions (table 1), the peak at 695 cm⁻¹ is unique to the crystalline materials. The bands around 1000 cm⁻¹ appears due to the silicon-oxygen stretching vibrations and the tetrahedral–tetrahedral ion vibrations affected the band around 780 cm⁻¹ for silicate, the tetrahedral dimensions are generally considered to be little affected by pressure and temperature. The absorption

Table 1. Characteristics of IR bands associated with quartz.

SiO ₄ tetrahedra	Type of IR band modes of vibration	Frequency (cm ⁻¹)
v3	Si–O asymmetrical stretching vibration	1080–1175
v1	Si–O symmetrical stretching vibration	780–800
v2	Si–O symmetrical bending vibration	695
v4	Si–O asymmetrical bending vibration	464

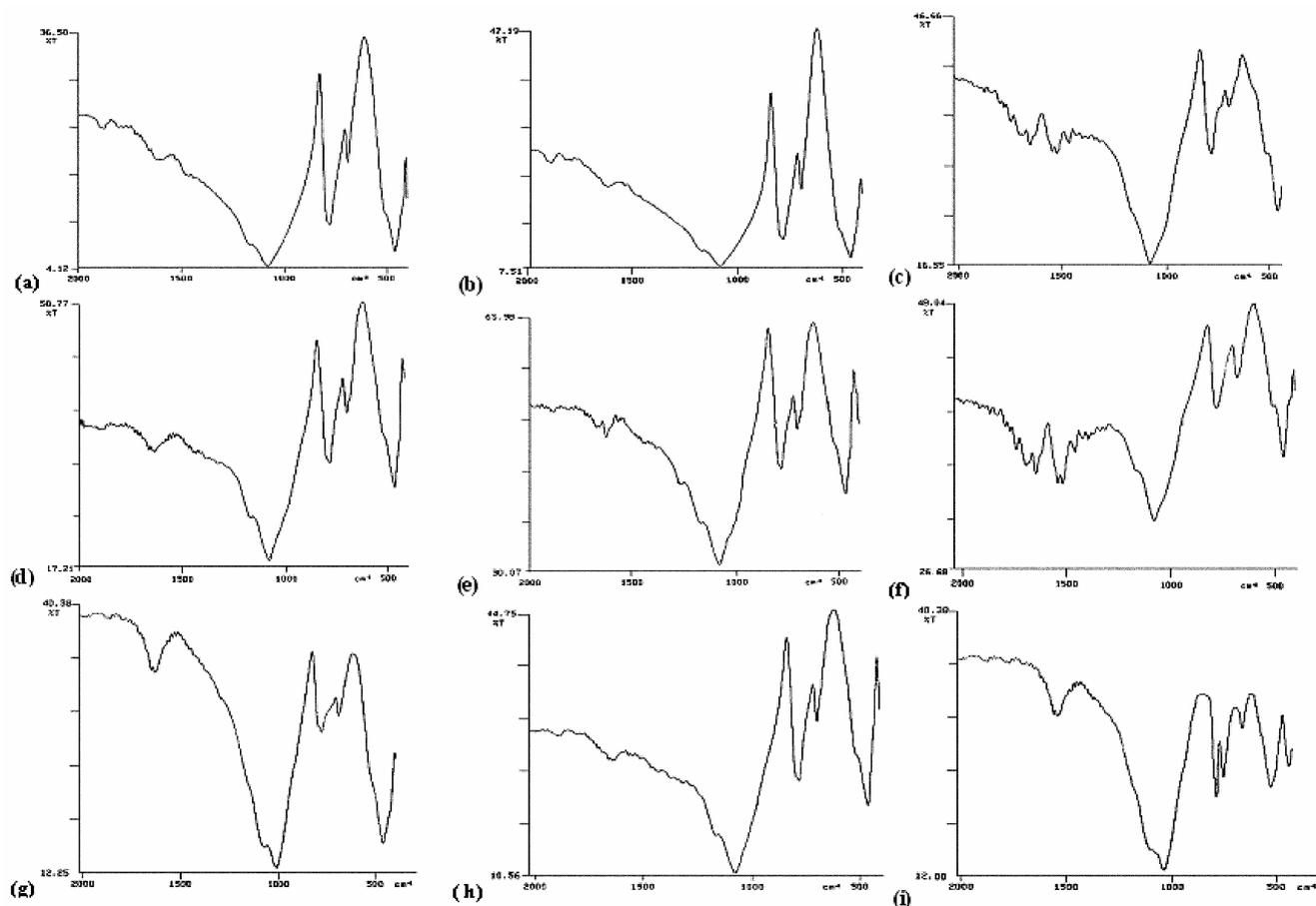


Figure 1. IR spectra of (a) Q-01, (b) Q-02, (c) Q-03, (d) Q-04, (e) Q-05, (f) Q-06, (g) Q-07, (h) Q-08 and (i) standard quartz in between 500–2000 cm⁻¹.

Table 2. IR frequencies for different samples are compared with standard quartz.

Sample	Frequency (cm ⁻¹)					
Quartz (Standard)	1085	800	780	695	514	462
Q-01	1081	–	780	692	–	461
Q-02	1083	–	780	692	–	460
Q-03	1082	–	778	691	512	459
Q-04	1083	801	780	692	514	458
Q-05	1082	797	782	694	524	462
Q-06	1081	–	781	694	514	457
Q-07	1083	800	780	691	–	461
Q-08	1081	800	778	693	512	458

band at 695 cm⁻¹ arises due to the octahedral site symmetry. The tetrahedral site symmetry is stronger to that of octahedral site symmetry. Therefore, for any structural change, the damage occurs first in octahedral site symmetry then in tetrahedral site symmetry. The intensity of the bands due to the vibrations of these two symmetries will provide direct information on the crystallinity. It is well known that in the infrared spectra of amorphous silica the symmetrical bending vibration of the Si–O group found at 695 cm⁻¹ is absent. Therefore, the symmetrical bending

vibrations of Si–O group obtained at 695 cm⁻¹ is diagnostic peak in determining the short range parameter of the quartz, whether it is crystalline or amorphous.

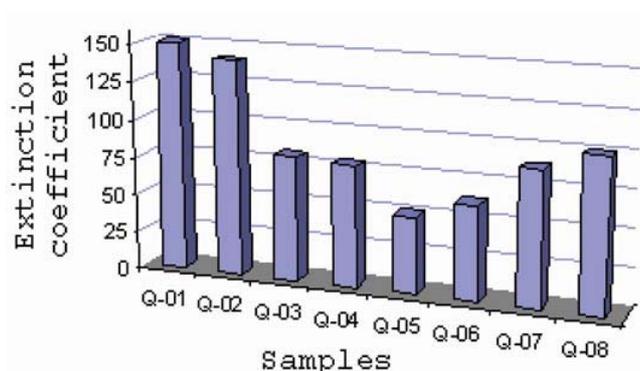
The characteristic of infrared bands associated with quartz is described in table 2, along with the normal modes of vibration of SiO₄ tetrahedra. The absorption bands located at ~650–440 cm⁻¹ and ~1000–850 cm⁻¹ involve atomic motions within the SiO₄ tetrahedra. The former frequencies represent asymmetric and symmetric Si–O bending vibrations, whereas the latter represent

Table 3. Percent crystallinity of quartz in various samples from FT-IR analysis.

Sample	778 cm ⁻¹ peak intensity (%T)	Intensity (Å)	695 cm ⁻¹ peak intensity (%T)	Intensity (Å)	Crystallinity index	Percent crystallinity
Quartz (Std.)	11.69	0.9329	22.84	0.6413	1.45	
Q-01	11.01	0.9582	19.22	0.7162	1.34	92.41
Q-02	12.58	0.9003	21.08	0.6761	1.33	91.72
Q-03	29.88	0.5246	35.48	0.4500	1.17	80.69
Q-04	30.86	0.5110	36.80	0.4342	1.18	81.38
Q-05	47.39	0.3243	53.76	0.2695	1.20	82.76
Q-06	39.75	0.4007	42.19	0.3748	1.07	73.79
Q-07	27.11	0.5669	28.59	0.5438	1.04	71.72
Q-08	22.77	0.6426	30.95	0.5093	1.26	86.90

Table 4. Extinction coefficient of quartz at around 778 cm⁻¹ peak for various samples.

Sample	778 cm ⁻¹ (%T)	Intensity of peak (<i>D</i>)	Optical density (<i>K</i>)	Extinction coefficient
Q-01		11.01	0.9582	150.44
Q-02		12.58	0.9003	141.35
Q-03		29.88	0.5246	82.36
Q-04		30.83	0.5110	80.23
Q-05		47.39	0.3243	50.91
Q-06		39.75	0.4007	62.91
Q-07		27.11	0.5669	89.00
Q-08		22.77	0.6426	100.89

**Figure 2.** Plot of extinction coefficient vs various quartz samples. The maximum extinction coefficient at 150.44 for the sample, Q-01 and minimum for the sample, Q-05 at 50.91.

asymmetric Si-O stretching vibrations (Geiger 1998). The infrared spectra of the studied samples in between 500–2000 cm⁻¹ are shown in figure 1. The frequencies of all the eight studied samples (table 2) can be assigned with reference to table 1. In table 2, we observed a slight shift in the position of the characteristic peaks at 778 and 695 cm⁻¹ which may be due to the associated minerals or crystal defects of the sample.

The infrared technique can be used to monitoring the crystallinity of silicate during paragenesis of the rock. To calculate the crystallinity index, the method applied here is the intensity ratio of the stretching mode at around 778 cm⁻¹ and the bending mode at around 695 cm⁻¹. Generally the symmetrical bending vibration of Si-O at

695 cm⁻¹ is identical for crystalline phase. The calculated ratio of 778 cm⁻¹ and 695 cm⁻¹ is interpreted in table 3.

To estimate the relative distribution of quartz among the studied samples, the extinction coefficient for the characteristic peak at 778 cm⁻¹ has been calculated. The extinction coefficient has been calculated using the relation

$$\text{Extinction coefficient (K)} = DA/m,$$

where *A* is the area of the pellet and *m* the mass of the sample. The optical density (*D*) is defined as the logarithm to the base 10 of the reciprocal of the transmitted radiant power (*T*).

From table 4 it can be seen that the intensity of the peaks is reciprocal to the extinction coefficient of the sample. This is also in agreement with the calculated values of optical density. The plot as referred to in figure 2 shows the samples versus extinction coefficient of the various samples. The availability of quartz among the various samples is determined by comparing extinction coefficient of the sample. The observation shows the maximum extinction coefficient at 150.44 of the sample, Q-01 and minimum of it for the sample, Q-05 at 50.91. Therefore, the sample, Q-01, is taken to have maximum quartz whereas the sample, Q-05, has minimum and between these two limits the quartz contaminants are distributed among the studied sample.

5. Conclusions

The infrared method is used for identifying the quartz in the rock samples of Mikir and Khasi hills, India. The cry-

stallinity of samples has been ascertained by comparing the ratio of intensity of the characteristic peak at 778 cm⁻¹ and 695 cm⁻¹ with the corresponding ratio for a standard sample. The observed crystallinity is responsible to the tetrahedral symmetry and octahedral symmetry of the 10 μm and 20 μm regions of the infrared spectra. We obtain a distribution of SiO₂ among the various rock samples by calculating the percent crystallinity. The crystallinity obtained from this infrared investigation represents the ratio of characteristic amorphous peak at 695 cm⁻¹ and the tetrahedral characteristic peak at 778 cm⁻¹ which is found to be good for structure elucidation. The presence of the 695 cm⁻¹ peak and the crystallinity provide that the SiO₂ mineral in all the samples are in crystallized form. From the value of crystallinity we can identify purity of the samples. The low value of crystallinity index indicates that the sample has a poor crystalline form which is indicative of the impurities during crystallization. The crystallinity index of quartz samples is important for mining industries, and environmental remediation.

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