Journal of Materials Physics and Chemistry, 2014, Vol. 2, No. 2, 28-33
Available online at http://pubs.sciepub.com/jmpc/2/2/3
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DOI:10.12691/jmpc-2-2-3

Spectroscopic Estimation of Geometrical Structure Elucidation in Natural SiO_2 Crystal

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Received October 31, 2014; Revised November 19, 2014; Accepted December 15, 2014

Abstract This study demonstrate for the first time the geometrical structure change relationship of natural quartz crystal structures with its purity through infrared spectroscopy. Systemetatic investigations of geometrical structure changes of the quartz crystals have been carried out in mid infrared region 500-1000 cm^{-1} based on the assignment of infrared bands of the structural group SiO_4 tetrahedra. The compositional and structural studies were carried out at room temperature by using X-ray fluorescence (XRF) and Fourier transform infrared (FTIR) spectroscopic techniques. The variation of geometrical structure of quartz crystals has been ascertained by comparing the infrared and X-ray fluorescence results. Results depict the variation of crystal size and shift of characteristic peak positions of the studied samples are depends on its purity. The infrared investigation is found to be good for structure elucidation and changes of geometrical crystal structures of the natural quartz crystals.

Keywords: *quartz crystal, infrared spectroscopy, XRF, structure elucidation*

Cite This Article: Bhaskar J. Saikia, "Spectroscopic Estimation of Geometrical Structure Elucidation in Natural SiO_2 Crystal." *Journal of Materials Physics and Chemistry*, vol. 2, no. 2 (2014): 28-33. doi: 10.12691/jmpc-2-2-3.

1. Introduction

Quartz is a pure mineral that has the chemical formula SiO_2 and is crystalline in structure. It cannot exist in slab form in a pure state. Quartz has a density of 2.649 g/cm^3 with trigonal crystal system in $D_3(32)$ crystallographic group. Quartz, or α-quartz, is the mineral form of SiO_2 stable at low temperatures and pressures. Quartz crystals changes from α to β quartz crystal at a temperature of 573°C because of phase transition. This phase transition is reversible, but transition from β quartz crystal to α crystal does not take place homogeneously. Quartz is colorless in its pure form, but due to trace minerals, many colors are found in nature. A quantitative analysis of trace elements in quartz crystals has been reported by many authors [1-5]. Quartz has an exceptionally stable atomic configuration of Si-O bonds that allows only a minimal amount of other elements into its structure. In addition to structural impurities, quartz frequently contains solid and fluid inclusions. It is always nearly pure silica with less than 0.2 percent of total impurities.

Information about structural defects in quartz crystals can be obtained from Fourier-transform infrared (FTIR) spectroscopy [6-11]. The crystal structure analysis discussed here is necessary to investigate the correlation between the trace oxide inclusions; characteristic infrared band shift and crystal face size in the crystal growth [12]. The actual mechanisms responsible for the variation in size and shape of individual crystal faces are, in fact, not well understood [13]. The major goal of this type of analysis is to understand the crystal growth mechanisms. In the present work we address the IR and XRF technique for estimation of geometrical structure studies of some selected quartz crystals of northeastern India.

2. Experimental

The estimation of the geometrical structures of the natural quartz crystals (Figure 1) is done by calculating the each crystal faces of the studied samples using slide calipers. Five independent measurements were carried out for each face of each sample and the average of the crystal faces of the samples is presented here.

A part of the samples was crushed into fine powder (75 μ) for analysis, by using agate mortar. The powdered samples (0.25 g) are put into platinum crucibles and HNO_3 (conc.), HCl, H_2O_2 and HF are added in a proportion of 5: 2: 1: 2 ml. Crucibles are heated on hot plate and the solution evaporated to near dryness. After that 2 ml HF are added few times until precipitate of SiO_2 is eliminated as SiF_4 vapors. After cooling down to the room temperature, a mixture of HCl (conc.) and redistilled water at a ratio 2: 5 ml is added, the solution transferred in 50 ml volumetric flasks and filled up with redistilled water. Then 0.5 g of powdered sample is put in a glass beaker and a mixture of redistilled water and HCl (conc.) in a ratio 15: 20 ml is added and the solution evaporated to near dryness. The residue is dissolved with 10 ml 1 % tin, and SiO_2 precipitated and coagulated. Precipitate is filtered and washed with HCl solution in a ratio 5:95 ml. Filter paper and residue are transferred into a platinum crucible and heated on 1000°C for 10 min. Crucible is weighed and the content of SiO_2 calculated. Then 0.5 g of powdered

sample is put in a glass beaker and a mixture of redistilled water and HCl (conc.) in a ratio 15: 20 ml is added and the solution evaporated to near dryness. The residue is dissolved with 10 ml 1 % tin, and SiO_2 precipitated and coagulated. Precipitate is filtered and washed with HCl solution in a ratio 5:95 ml. Filter paper and residue are transferred into a platinum crucible and heated on 1000°C for 10 min. Crucible is weighed and the content of SiO_2 calculated.

The powdered sample was homogenized in spectrophotometric grade KBr (1:20) in an agate mortar and was pressed 3 mm pellets with a hand press. We tried to minimize the grinding time to avoid the deformation of the crystal structure, the ion exchange and the water absorption from atmosphere. The infrared spectra 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 31°C during the experiment.

The composition of the quartz crystals was determined by using Philips X-ray fluorescence (XRF) machine. The method of sample preparation for investigation is discussed elsewhere [14,15,16]. Five independent measurements were carried out and the average composition of the sample is presented here. The chemical composition of the samples was also observed by electron probe micro-analyzer (EPMA). Energy Dispersive X-ray (EDX) measurements were carried out by using scanning electron microscope (JEOL JSM - 840 A) in EDX mode with a filament current of 100 μA and an accelerating voltage of 20 kV probe current 45 nA and counting time 60 seconds. Polished thin sections were investigated for the elemental composition. The calibration and reproducibility of this apparatus is discussed elsewhere [17]. In X-ray fluorescence method, typical uncertainty involved in oxide analyses was about 0.01 wt%.

3. Results and Discussion

The characteristic of infrared bands associated with quartz crystals are in the range of 1200-400 cm^{-1} [18]. In the studied samples the SiO_4 tetrahedra exhibits Si–O asymmetrical stretching vibration (*v3*) in between 1175-1080 cm^{-1}, Si–O symmetrical stretching vibration (*v1*) in between 784.11-779.11 cm^{-1}, Si–O symmetrical bending vibration (*v2*) in between 696.21-694.44 cm^{-1}, and Si–O asymmetrical bending vibration (*v4*) in between 466-463 cm^{-1} (Figure 2). The peak at 695 cm^{-1} arises due to the octahedral site symmetry and is unique to the crystalline materials. The tetrahedral-tetrahedral ion vibration affects the band at 778cm^{-1} in silicates, the tetrahedral dimension is generally considered to be little effected by pressure and temperature [19-22]. 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 and crystal growth. 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 missing [20,21,22]. 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. We focused on these characteristic peaks 778 and 695 $cm^{-1}$of each samples to investigate the purity and structural relationship.

Table 1. Chemical compositions (%wt) and amount of trace oxides or contaminations (%wt) of the studied quartz crystals

Sample	Composition (wt%)								Amount of trace oxides /contamination (%wt)
	SiO_2	Al_2O_3	FeO	MgO	CaO	K_2O	TiO	MnO	
Q-01	99.79	0.14	0.06	--	--	--	0.003	0.005	0.21
Q-02	99.73	0.18	0.05	--	0.02	0.01	--	0.001	0.27
Q-03	99.76	0.13	0.09	0.001	0.01	--	0.001	--	0.24
Q-04	99.41	0.35	0.04	0.007	0.07	0.01	0.005	0.011	0.59
Q-05	99.49	0.21	0.14	--	--	0.06	0.009	0.010	0.51
Q-06	99.59	0.27	0.09	0.005	0.01	--	0.003	0.001	0.41
Q-07	99.65	0.25	0.05	--	0.01	0.02	0.001	--	0.35
Q-08	99.69	0.17	0.12	0.002	--	--	0.001	0.003	0.31
Q-09	99.48	0.23	0.11	--	--	0.07	0.006	0.011	0.52
Q-10	99.61	0.12	0.20	--	0.02	--	0.008	--	0.39
Q-11	99.71	0.13	0.09	0.040	0.01	--	0.001	--	0.29
Q-12	99.67	0.16	0.10	0.001	--	0.04	0.003	0.005	0.33

The chemical composition and purity level of the samples are depicted in the Table 1 and Table 2 respectively. The XRF result (Table 1) reveals 99.79 percent of SiO_2 compositions with low grade of trace oxide of 0.21 percent in sample Q-01 and its size of average crystal faces are found to be the maximum value 1.4652 cm among the studied samples. In nearly pure silica, less than 0.2 percent of total impurities are generally observed. The impurity level of the sample Q-1 is found to be almost equal to the standard level of impurity. The crystallinity index of samples has been ascertained by the ratio of intensity of the characteristic peak at 778 cm^{-1} and 695 cm^{-1} and percent crystallinity is calculated by considering crystallinity index of Q-1(1.34) as standard whose impurity level is found to be lowest among the samples (Table 1). Generally the symmetrical bending vibration of Si–O at 695 cm^{-1} is identical for crystalline phase. The calculated percent crystallinity and corresponding value of SiO_2 composition of each sample are interpreted in Table 2 [22]. The low value of

crystallinity index indicates that the sample has a poor crystalline form which is indicative of the impurities during crystallization. The intensity and position of these characteristic infrared peaks are affected by the inclusion. However, the inclusion affects the growth of the crystal size. Therefore, the correlations among crystallinity, inclusion and crystal faces are indicative measure of the purity of the quartz crystals. Generally the theoretical difference of tetrahedral and octahedral site symmetry is 83 cm^{-1}. The characteristic peaks positions (778 and 695 cm^{-1}) of the studied samples are described in the Table 3., and is vary with contaminations which affect the size of the crystals in its natural growth. The change of average crystal faces is calculated by considering the maximum size of average crystal faces of Q-1 (1.4652 cm) as standard.

Comparative evaluation of XRF and IR results shows almost similar estimation values for percent of SiO_2 composition and percent crystallinity with each other for all samples (Table.2). The Table 2 also depicts the variation of crystal faces/size with purity level of the crystals. The maximum infrared peak shift 6.08 cm^{-1} is observed in the sample Q-04 with maximum trace oxide and SiO_2 compositions 0.59 %wt and 99.41 %wt. respectively. Similarly the minimum infrared peak shift 1.29 cm^{-1} is observed in the sample Q-01 with minimum trace oxide and SiO_2 compositions 0.21 %wt and 99.79 %wt. respectively. The crystallinity of the samples are calculated by considering the sample Q-01 taken as standard since it has less peak shift and minimum trace oxide. The infrared result shows the crystallinity are 100 % and 87.31% respectively for the samples Q-01 and Q-04.

It is well known that temperature and pressure influences the growth of quartz crystals. Apart from pressure and temperature, the sizes of the naturally occurring quartz crystals are affected by its trace composition. It is emphasized that the geometrical size of the natural quartz crystal can be considered one of the indicators of purity. The composition of the trace oxides are also affects the purity as well as the intensity of the characteristic infrared peaks of the samples. Table 2 signify that the intensity of the infrared characteristic peaks are found to be maximum in the sample Q-01 in which the corresponding trace oxides are have a marginal value.

Table 2. Percent transmittance of tetrahedral and octahedral peaks (%T), tetrahedral and octahedral peak intensities (Å), crystallinity index, percent crystallinity index, and composition of SiO_2 (%wt) among the studied quartz crystals

Sample	Composition (wt%)								Amount of trace oxides /contamination (%wt)
	SiO_2	Al_2O_3	FeO	MgO	CaO	K_2O	TiO	MnO	
Q-01	99.79	0.14	0.06	--	--	--	0.003	0.005	0.21
Q-02	99.73	0.18	0.05	--	0.02	0.01	--	0.001	0.27
Q-03	99.76	0.13	0.09	0.001	0.01	--	0.001	--	0.24
Q-04	99.41	0.35	0.04	0.007	0.07	0.01	0.005	0.011	0.59
Q-05	99.49	0.21	0.14	--	--	0.06	0.009	0.010	0.51
Q-06	99.59	0.27	0.09	0.005	0.01	--	0.003	0.001	0.41
Q-07	99.65	0.25	0.05	--	0.01	0.02	0.001	--	0.35
Q-08	99.69	0.17	0.12	0.002	--	--	0.001	0.003	0.31
Q-09	99.48	0.23	0.11	--	--	0.07	0.006	0.011	0.52
Q-10	99.61	0.12	0.20	--	0.02	--	0.008	--	0.39
Q-11	99.71	0.13	0.09	0.040	0.01	--	0.001	--	0.29
Q-12	99.67	0.16	0.10	0.001	--	0.04	0.003	0.005	0.33

Table 3. The tetrahedral and octahedral frequencies (cm^{-1}), theoretical and observed differences of tetrahedral and octahedral frequencies (cm^{-1}), size of average crystal faces (cm), and change of average crystal face (cm) among the studied quartz crystals

Sample	Characteristic infrared frequencies		Observed difference of Tetrahedral & Octahedral peak (cm^{-1})	Theoretical difference of Tetrahedral & Octahedral peak (cm^{-1})	Observed and theoretical peak shift (cm^{-1})	Size of average Crystal faces (cm)	Change of average crystal face (cm)
	Tetrahedral (778cm^{-1})	Octahedral (695cm^{-1})					
Q-01	779.42	695.13	84.29	83	1.29	1.4652	0
Q-02	780.51	696.21	84.30	83	1.30	1.4175	0.477
Q-03	779.23	694.89	84.34	83	1.34	1.3361	1.291
Q-04	784.11	695.03	89.08	83	6.08	0.8273	6.379
Q-05	782.43	695.21	87.47	83	4.47	0.9479	5.173
Q-06	783.23	696.01	87.22	83	4.22	1.0754	3.898
Q-07	779.87	694.92	84.95	83	1.95	1.0542	4.110
Q-08	779.46	694.44	85.02	83	2.02	1.2391	2.261
Q-09	781.55	695.26	86.29	83	3.29	0.9883	4.769
Q-10	779.27	694.49	84.78	83	1.78	1.0747	3.905
Q-11	779.11	694.75	84.36	83	1.36	1.1533	3.119
Q-12	780.32	695.38	84.94	83	1.94	1.1416	3.236

The shift of the characteristic peaks of each samples are ascertain from the theoretical peak difference of 778 and 695 cm^{-1}. The variation of the average crystal face is estimated from the maximum face size of sample Q-01. Table 3 infers the shift of the characteristic peaks and variation of the geometrical crystal structure respectively. The shift of peak positions in the tetrahedral and octahedral site symmetry indicates the effect of trace minerals or oxides associated with the quartz crystal during the crystal growth or formation. The trace ion oxide or elements are responsible for the colour variation of the quartz crystals. The milky white colour of quartz minerals is due to the presence of traces of Ca, the appearance of black colour is the result of the existence of

Pb, Mn and Al impurities, and the occurrence of red and green colour is due to Fe, Ti and Cr trace impurities respectively. The smoky colour of quartz may also cause by low levels of ionising radiation induced by the decay of radioactive elements in neighbouring minerals (e.g. ^{40}K in alkali feldspar) [23]. The selected samples are almost transparent with light colour variation (Figure 1).

The plot exhibits that, as the presence of trace oxides in the quartz samples decreases the average crystal faces are increases with a very strong correlation ($R^2 = 0.9185$). The change of position in the infrared characteristic peaks are also inversely proportional to the size of average crystal faces of the studied crystal with a strong correlation ($R^2 = 0.8177$). However, the value of crystillinity index in the observed crystals has directly proportional to the size of average crystal faces of the crystals (Figure 3). The value of crystillinity index and the size of average crystal faces of the crystals are depicts a strong correlation ($R^2 = 0.8132$).

The strong correlation ($R^2 = 0.837$) between the trace oxide or contaminations with the changes of infrared characteristic peaks positions exhibits that the change of position in the infrared characteristic peaks are directly related to the trace oxide or contaminations of the quartz crystals. The value of characteristic infrared peak shift is increases with increasing of the value of trace oxides in the sample. The values of crystallinity indices are decreases as increasing the value of trace oxides or contaminations. It also affects the infrared characteristic peak shifts, the infrared characteristic peak shift decreases as the value of crystallinity indices are increases (Figure 3).

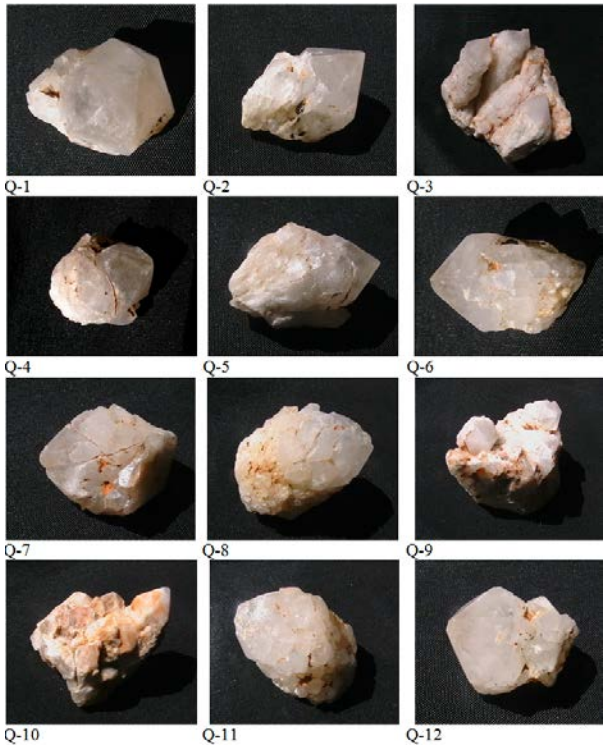

Figure 1. Photograph of studied quartz crystals

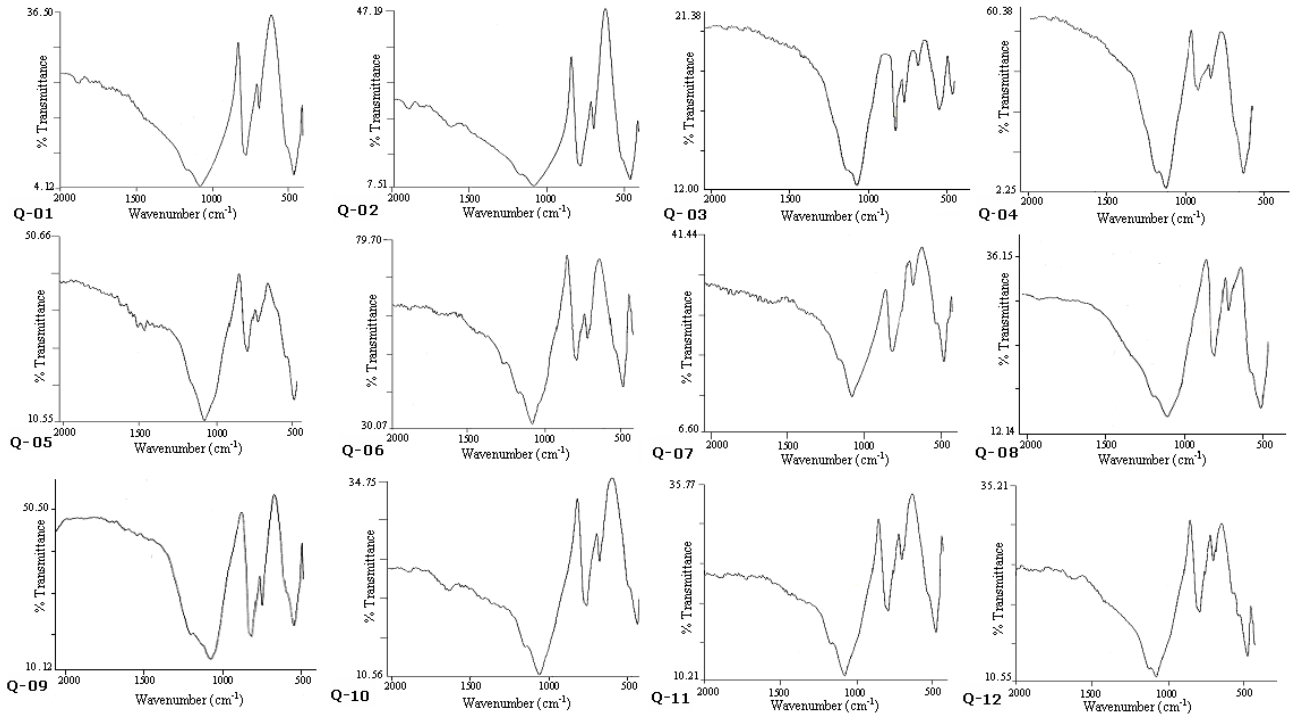

Figure 2. FTIR spectra of the studied quartz crystal samples in the finger print region

The of changes in average crystal faces size of the observed crystals with the value of trace oxides concentrations and the change of position in the infrared characteristic peaks are directly proportional to each other with same correlation values with that of the size of the average crystal faces. The values of crystallinity index and changes in average crystal faces size exhibits same correlation values with that of average crystal faces size, but in reverse order (Figure 3).

4. Conclusion

We observed the shift of infrared characteristic peaks is directly related to the trace oxide or contaminations of the sample. The average crystal faces of the samples are decreases with increasing the trace oxide or contamination concentrations. Likewise, the shift of infrared

characteristic peaks is increases with increasing of trace oxide or contamination concentrations. It is found that the highest value of trace oxide or contamination exhibits maximum peak shift. The trace oxide or contamination concentrations are strongly correlated with average crystal faces, crystallinity index and shift of the infrared characteristics peak with a strong correlation value 0.9185, 0.8231 and 0.8370 respectively. The shift of tetrahedral-octahedral site symmetry bands with the size of crystal faces of the quartz crystal throws light on the crystal growth and pressure-temperature (phase transition) during the process of formation. The variation of the associated trace oxides / minerals represents a good for structure elucidation and changes of geometrical shape of the quartz crystals. The IR, XRF and crystal faces measurement represents a quite comparable significant effect of trace level impurities in the process of crystal growth. Hence it can be conclude that the IR method can be used for monitoring the compositional relationship of quartz crystal growth.

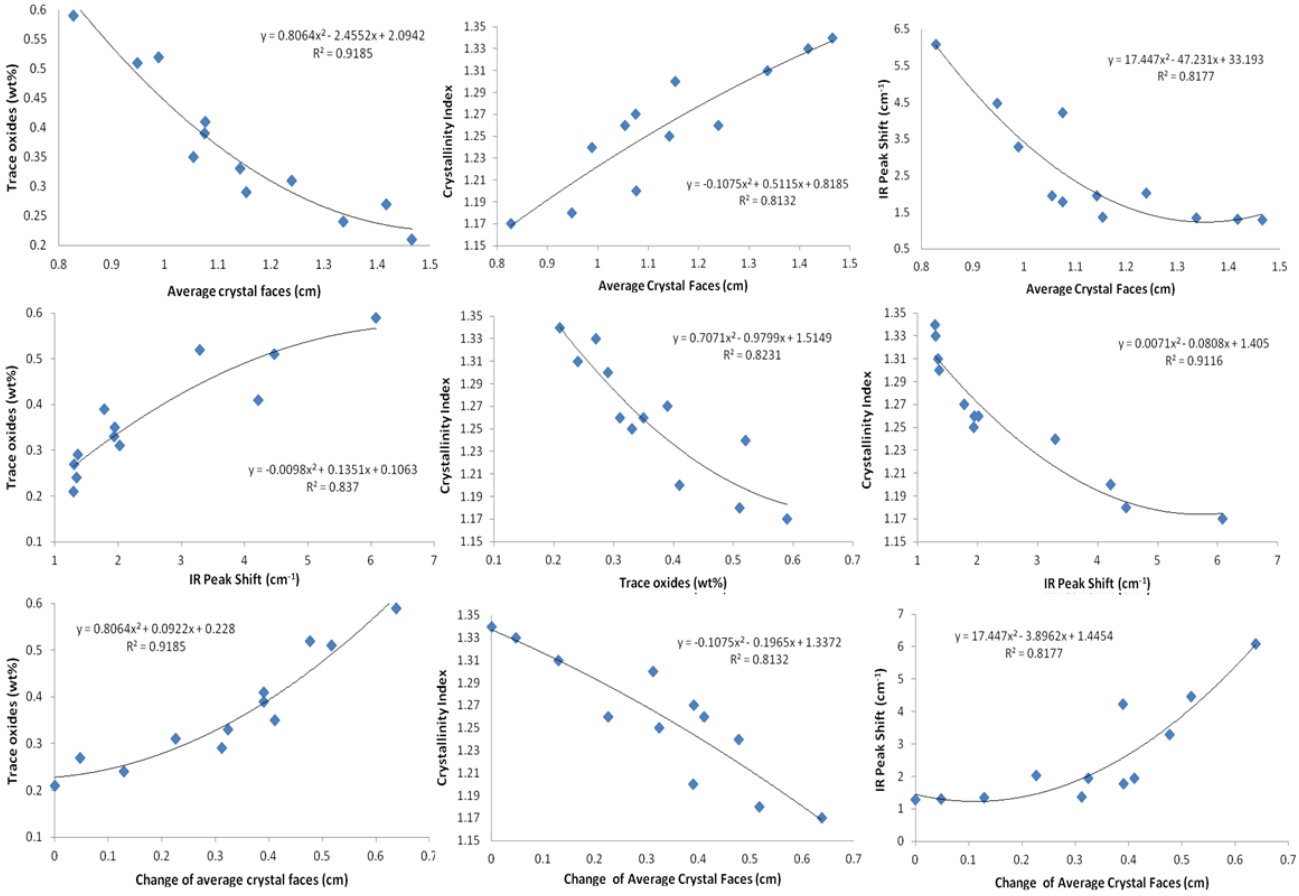

Figure 3. Correlations of different investigated factors of the studied quartz crystals

Acknowledgements

I thank Directors, National Geophysical Research Institute (NGRI-CSIR), Hyderabad and North East Institute of Science and Technology (NEIST-CSIR), Jorhat for their cooperation during this work. I also thank Dr. G. Parthasarathy, National Geophysical Research Institute (NGRI-CSIR), Hyderabad for his suggestion during the work and Dr. J.R. Chetia, Dibrugarh University, Dibrugarh, for his assistance in the FTIR analysis.

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