Infrared Absorption Spectra of Quartz and Some other Silica Modification

By Reisuke SODA

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Recently it was reported that the surface of a quartz particle was forced to change its structure by grinding[3-5]. Infrared absorption spectra of the quartz perticle showed that the band near 950 cm^{-1} appeared as the result of grinding and disappeared when the particle was leached[1,2]. The origin of the band near 3400 cm^{-1} was assumed to be the stretching vibration of O–H bond and its intensity changed depending upon the treatment of the particle. The parallel relation was observed between the intensity of 3400 cm^{-1} band and that of 950 cm^{-1}. The intensities of the two bands increased with the degree of grinding. Another silica modification such as carplex gave rise to the 950 cm^{-1} band and the intensities of both the 950 cm^{-1} band and the 3400 cm^{-1} band of this compound were stronger than those bands of other silica modifications. Previously the author assigned it tentatively to the deformation vibration of O–H link of silanol group at the surface layer of the particle[1]. In the present paper more evidence will be given to confirm the assignment of this band.

Experimental

A quartz sample was prepared by grinding and in some cases by leaching the ground particle. The ground particle was fractionated by the particle size suspending it in water and separating it with centrifugal force. This procedure was reported in the other paper[1]. Ten per cent aqueous solution of sodium hydroxide was used to leach the particle. A quartz sample used was that was produced at Ishikawayama. The carplex was supplied by the Shionogi Co., Ltd. It was fine powder of particle size less than 0.5 μ. The sample powder was mixed with potassium bromide in an agate mortar. The potassium bromide used was c. p. grade and pulverized in agate mortar into particle size of 200 to 300 mesh by sieving with a stainless steel sieve and dried by heating above 200°C for about one day. The mixed powder was dried by heating at about 150°C for 3 hr. and poured into the die to be pressed under 10 tons per square centimeter after evacuation for about 10 min. A shaped disk was inserted into the cell for the potassium bromide disk method.

Infrared absorption spectra were measured with Perkin-Elmer model 137 infracord spectrophotometer and Perkin-Elmer model 221 spectrophotometer.

Notations showing kinds of sample particles are as follows[1]:

Q-I-2M is the sample Ishikawayama quartz ground for 2 min., Q-I-6H that ground for 6 hr., Q-I-24H for 24 hr., O-I-100H for 100 hr. and Q-I-2M-L is the sample Ishikawayama quartz ground for 2 min. and leached with aqueous sodium hydroxide.

Results

The spectrum of Q–I–2M gives rise to the bands at 1180, 1150 and 1070 cm^{-1}. These are very strong, but those at 800, 780 and 695 cm^{-1} are sharp and have medium intensities. Sometimes a band near 3400 cm^{-1} is observed with only a very weak intensity. The spectrum of Q–I–6H gives rise to the very weak band at 950 cm^{-1} and to a weak but clear band at 3300 to 3400 cm other than those of Q–I–2M. In

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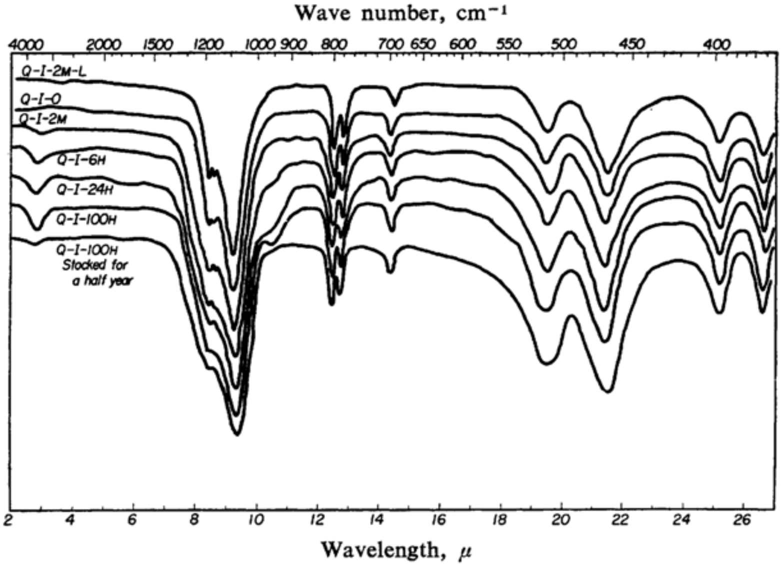

Fig. 1. Spectra of quartz particles prepared by various procedures. The range of particle size is $0.5\sim2\,\mu$ and mean size is about $1\,\mu$. Samples are Ishikawayama quartz ground by hand (Q-I-0), ground mechanically for 2 min. (Q-I-2M), for 6 hr. (Q-I-6H), for 24 hr. (Q-I-24H) and for 100 hr. (Q-I-100H). Q-I-2M-L designates Ishikawayama quartz ground for 2 min. and leached by NaOH aq.

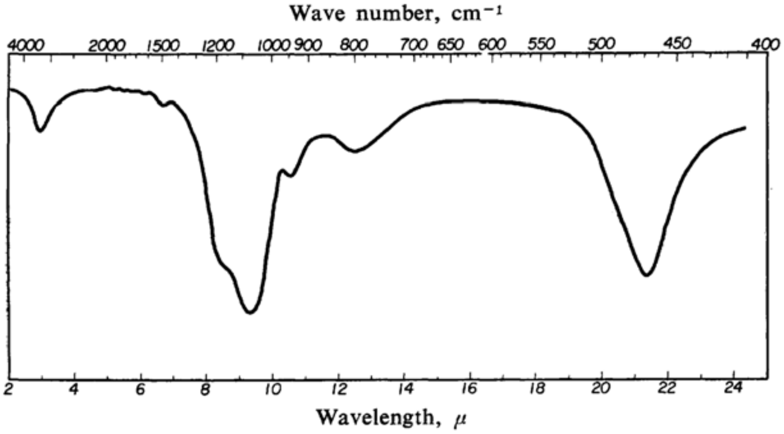

Fig. 2. Spectrum of amorphous silica "Carplex".

spectra of Q-I-24H and Q-I-100H the bands at 3300 to 3400 cm^{-1} and at 950 cm^{-1} are more intense than those of Q-I-6H. The intensities of those bands increase with grinding times. In the spectrum of Q-I-100H which has been kept in a desiccator for a half year, the intensities of the bands at 3400 and 950 cm^{-1} decrease and sometimes the band at 950 cm^{-1} is scarcely observed. The spectrum of carplex gives rise to the strongest bands at 1160 and 1090 cm^{-1} and to a very weak broad band near 800 cm^{-1}. Besides those bands, it gives rise to a band of medium intensity at 3300 cm^{-1} and to a well defined band near 950 cm^{-1} as shown in Fig. 2.

The spectrum of Q-I-2M-L gives rise to no bands at 3400 and 950 cm^{-1}. The three bands near 1100 cm^{-1} changed their aspects with their grinding times and with leaching. These band groups are sharply separated with leached quartz and lose their defined aspects with the grinding process. The band at 1070 cm^{-1} is broader and first the band at 1150 cm^{-1} becomes like the shoulder of 1070 cm^{-1} band and finally is masked by the latter band with the increment of grinding time. The band at 1180 cm^{-1} is like the shoulder of 1070 cm^{-1} band also when the grinding time is longer than about 20 hr. These changes are illustrated in Fig. 1. In the region of the cesium bromide

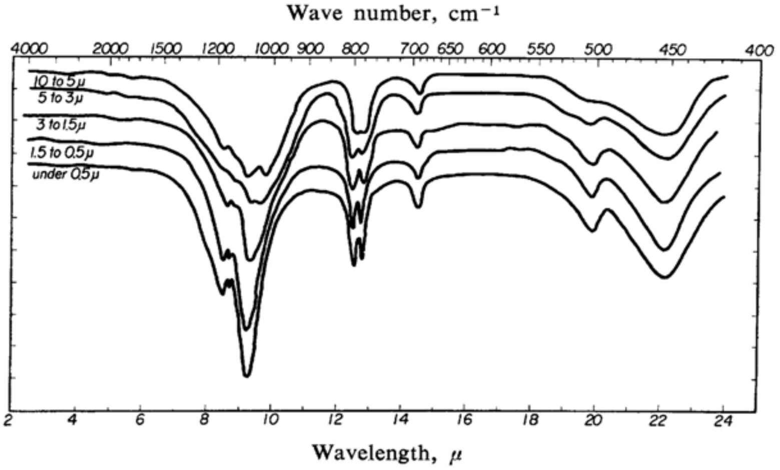

Fig. 3. Spectra of quartz in several range of particle size. Sample is Ishikawayama quartz ground for 2 min. and leached by NaOH aq.

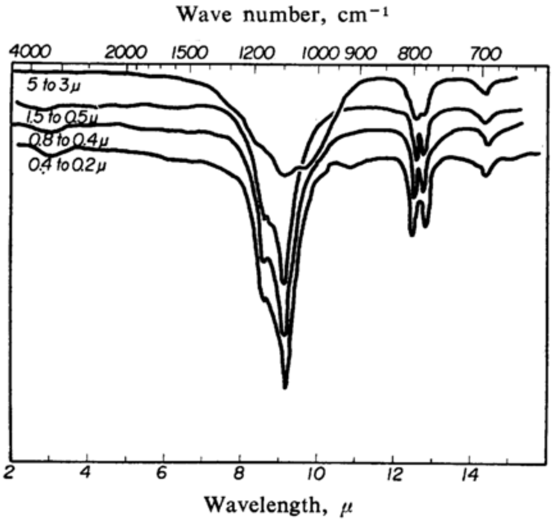

Fig. 4. Spectra of quartz in several range of particle size. Sample is Ishikawayama quartz ground for 100 hr.

optics, the spectrum of quartz powder is not influenced by the grinding times.

The spectrum of quartz powder changes its aspect with particle size in several regions. These changes are shown in Figs. 3 and 4. Figure 3 illustrates the spectra of Q-I-2M-L samples which have the particle size of the order of ten to zero microns. Figure 4 illustrates the spectra of Q-I-100H samples stocked for a half year, the particle sizes of which are from the order of 10 to that of 0.2 μ. The particle size has a remarkable influence on the spectrum in the region of 8 to 9 μ, and less remarkably on those in the regions of 12 and 20 μ. Particularly this effect is markedly seen when the particle size is larger than 3 μ. These results are summarized in Table I.

Discussion

In general, silica modifications give rise to strong bands in the region of 1200 to 1050 cm^{-1}. These bands may be assigned to stretching vibration of Si-O[6,7]. The bands at 800, 780 and 694 cm^{-1} of quartz are also attributed to the silica structure and are very sensitive to skeletal structure of silica. In the longer wavelength region of cesium bromide optics, the bands at 519, 470, 398 and 376 cm^{-1} are attributed to the vibrations concerned with skeletal structure. Beyond those bands, the bands at 3400 and 950 cm^{-1} which appear in the spectrum of carplex, Q-I-6H, Q-I-24H and Q-I-100H are not attributable to the abovementioned structure sensitive vibrations but may be assigned mainly to hydroxyl group vibration of the silanol group[8-10]. Particle size has a very appreciable influence on the spectrum in the region of 8.5 to 9 μ and less but an effect which cannot be neglected on that in the region of 12 and 20∼24 μ particularly when the particle size is larger than 3 μ. These phenomena have been observed by several investigators and explained in a few ways[11]. At present the author has little interest in these explanations of the phenomena,

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TABLE I. INFRARED ABSORPTION BANDS AND THEIR CHARACTERISTICS OF SILICA

Band positions cm^{-1}	Remarks
3400 to 3300	Band intensity: strong to weak; carplex, Q-I-100H, Q-I-24H, Q-I-6H, Q-I-2M and Q-I-2M-L. Generally assigned to O-H stretching.
1180, 1150 and 1070	Very strong band region of quartz. The sharp feature with Q-I-2M and Q-I-2M-L is lost and the broadth of 1070 cm^{-1} band develops with grinding; 1150 cm^{-1} band appears as shoulder of 1070 cm^{-1} band with Q-I-6H and Q-I-24H, the former being covered by the latter with Q-I-100H. 1180 cm^{-1} band also appears as the shoulder of 1070 cm^{-1} band. Particle size influences features of these bands, and a new band occurs at 1040 cm^{-1} and this shifts towards lower wave number side as the particle size is larger than 3 μ. In that case, this band group is diffuse and seems to be less intense.
1160 and 1090	Very strong band with carplex.
Close to 950	Intensity: medium to weak; carplex, Q-I-100H, Q-I-24H, and probably Q-I-6H. This band cannot be found out with Q-I-2M and Q-I-2M-L.
800	Broad weak band with carplex.
800, 780 and 694	Characteristic bands of quartz with medium intensity. No appreciable change in the feature is observed by grinding. Particle sizes larger than 3 μ have an influence on the aspects of bands at 800 and 780 cm^{-1} but no influence on 694 cm^{-1} band.
520, 470, 400 and 380	Characteristic bands of quartz. No appreciable change occurs with grinding. Particle size influences their aspects as it is larger than 3 μ.

but would like to remark on the fact that as the particle size of ground quartz is smaller the band at 950 cm^{-1} is more intense and the band group in the region of 8 to 9 μ is more diffuse. This will be concerned in the considerably irregular structure different from the original quartz structure. These aspects are illustrated in Figs. 3 and 4.

From spectral change with grinding and leaching as illustrated in Fig. 1, it may be recognized that the bands at 3400 and 950 cm^{-1} also change their aspects in parallel. These two characteristic bands increase their intensities with the grinding times, decrease during the stock of sample in desiccator under the reduced pressure and disappear when the particle is leached. The relative intensity of these two bands scarcely differs with the samples treated in various ways.

It is generally accepted$^{3-5)}$ that quartz particle ground mechanically has a disturbed and easily soluble layer around the surface, the structure of which is different from quartz itself but not completely amorphous like silica gel. In this case it was observed by means of the BET method with argon or krypton that the surface area of particles increases with the grinding. The interior parent structure does not change its original structure during the grinding but the surface layer is gradually disturbed and the amount of disturbed layer or the thickness of this layer increases with grinding times. The leached sample decreases its surface area and it is considered that the spectrum of this sample is essentially the same as those of the original sample. The change of spectrum in the region of 8 to 9 μ is responsible for this disturbed structure on the particle surface. The more disturbed the layer is, the more diffuse bands appear in this spectral region. This will be caused by the superposition of the spectrum of the disturbed layer on the original spectrum$^{1)}$. According to the above consideration, it is concluded that the intensities of the bands at 3400 and 950 cm^{-1} increase with the increment of the amount of the disturbed layer surrounding the surface of the particle. The more the surface area increases, the more the number of SiOH bonds appears. Therefore the SiOH bonds exist mainly on the particle surface, particularly in the disturbed structure. The band at 3400 cm^{-1} which is assigned to the stretching vibration of OH bond will increase its intensities not only with the SiOH group but also with the absorbed water molecule. But the absorbed water molecule gives rise to the bands near 1600 cm^{-1} and does not at 900 to 1000 cm^{-1} generally$^{10)}$. From this consideration, the band at 950 cm^{-1} may be assigned to O-H deformation vibration of silanol group.

In the lower frequency region on new band was observed by the grinding. Therefore it is inadequate to consider that the band at 950 cm^{-1} be assigned to the overtone or combination tone. This argument supports indirectly above assignment of the band at 950 cm^{-1} to O-H deformation vibration. From the result of spectra obtained in this work, the band at 950 cm^{-1} may be reasonably assigned to the

O–H deformation vibration of silanol group on the surface of ground quartz particle.

Summary

Some silica modification such as carplex and ground quartz particle, gives rise to the bands near 950 cm^{-1}. This band has no relation with the skeletal structure of Si–O bond and can not be explained as overtone or combination tone. It is reasonable to assign this band to O–H deformation vibration of silanol group. The effect of particle size and grinding time on the spectrum of quartz was examined and it was concluded that the ground quartz particle was covered by some irregular structure on its surface, which was different from quartz structure. In this surface structure, the silanol group seems to be constructed.

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National Institute of Industrial Health
Kawasaki-shi, Kanagawa-ken