

The infrared absorption band at 3596 cm^{-1} of the recrystallized quartz from Mt. Takamiyama, southwest Japan

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ABSTRACT

Micro-FTIR (MFTIR) measurements were carried out on the natural recrystallized quartz in Ryoke granites from Mt. Takamiyama. The recrystallized quartz always shows a very strong IR absorption band at 3596 cm^{-1} (2.10 abs. cm^{-1} (normalized absorbance) under unpolarized conditions at room temperature). However, naturally deformed quartz does not show this absorption band, but only a characteristic broad band centred at 3400 cm^{-1} . This shows that the predominant forms of H-related species in the recrystallized quartz are different from those in naturally deformed quartz. The 3596 cm^{-1} band is not affected by room-temperature X-ray irradiation or by annealing at temperatures of up to 600°C , and shows broadening and a positive peak shift with temperature in *in situ* high temperature measurements. Polarized-MFTIR measurement shows that the band has a strong polarization; the OH dipole is oriented at 35° to the *a*-axis in the $(10\bar{1}0)$ plane and is isotropically distributed in the (0001) plane. From the stability of the band at high temperatures and against irradiation and its sharpness, the band is considered to be due to the Al(H) type point defect with no alkali which might occupy a structural position in the quartz structure.

KEYWORDS: IR, recrystallized quartz, hydrogen-related species.

Introduction

THERE have been several investigations on H and H-related species in various kinds of quartz (e.g. Griggs and Blacic, 1965; Griggs, 1967, 1974; Blacic, 1975; Kekulawala *et al.*, 1978; Paterson, 1989). Their results reveal that the H and H-related chemical species significantly affect the mechanical properties of quartz and that the species promote its recrystallization (Hobbs, 1968). Hydrogen coupled with Al substituted for Si, as a charge-compensate, can be incorporated into the quartz structure to maintain electrical neutrality. Kats (1962) suggests that the sharp absorption bands of quartz in the $3\text{ }\mu\text{m}$ IR region are due to the O–H stretching vibrations and that the great variety of sharp bands are essentially attributed to the Al substitutions and coupled charge-compensating alkali cations.

However, most of the previous works have been limited to large single crystals of synthetic quartz and natural, clear, vug-grown quartz as well as amethyst. Few studies have been carried

out on natural fine-grained quartz in rocks which have had a complex geological history, involving both deformation and recrystallization. The combination of an IR spectrometer with an optical microscope (MFTIR) makes it possible to analyse minor and trace amounts of H-related chemical species in rock-forming minerals at a grain by grain or point to point scale in rock thin section. Maki (1992) reports that a characteristically strong absorption band at 3596 cm^{-1} is observed in the recrystallized quartz from Ryoke granites, southwest Japan, which were annealed by the intrusion after deformation. The 3596 cm^{-1} band, which has not previously been assigned, is not a prominent band in most kinds of quartz, e.g. amethyst, synthetic quartz, or in synthetic quartz which has been reported previously (e.g. Chakraborty and Lehmann, 1976*a,b*; Rovetta *et al.*, 1989; Kats, 1962; Pankrath, 1991). Here we report that the naturally recrystallized quartz from the granite has a strong absorption band at 3596 cm^{-1} . This granite experienced its first deformation due to the

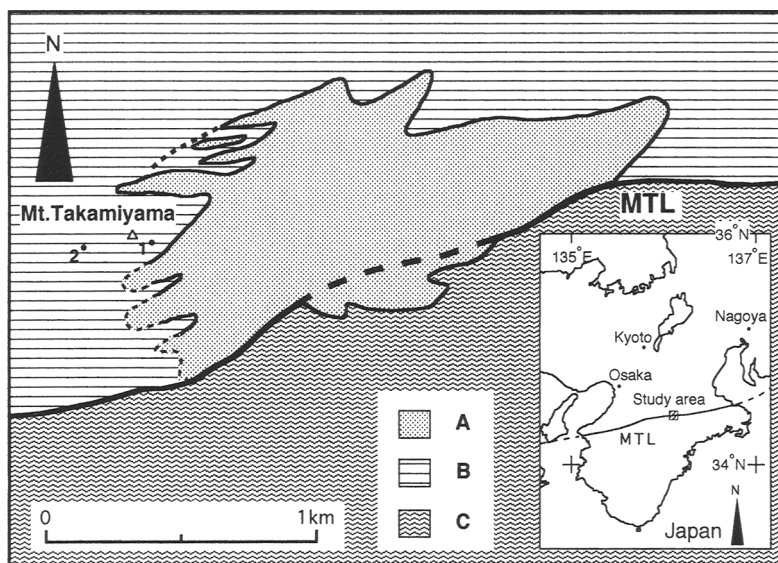


FIG. 1. Generalized geological map of the area around Mt. Takamiyama (compiled and partly modified from Ohira, 1982 and Shibata *et al.*, 1988). A – Takamiyama acidic rock; B – Ryoke granitic rocks; C – Sambagawa metamorphic rocks. Black filled circles with number represent sample localities. Recrystallized quartz from No. 1 and deformed quartz from No. 2, respectively.

Median Tectonic Line (MTL) movement and was annealed later by the intrusion of Takamiyama acidic rock body. To characterize the 3596 cm^{-1} band observed in the recrystallized quartz, we carried out room temperature FTIR measurements under unpolarized and polarized conditions, X-ray irradiation and annealing experiments, and *in situ* high temperature FTIR measurement. On the basis of the results and by comparing them with the other types of quartz previously studied, we discuss the assignment of the 3596 cm^{-1} band.

Geological setting

Mount Takamiyama is located at the border between Nara and Mie Prefectures in the central part of Kii Peninsula, southwest Japan (Fig. 1). Ryoke granitic rocks are distributed in the northern part of the study area, and are in contact with Sambagawa metamorphic rocks along the MTL (Fig. 1). The Ryoke granite in the study area belongs to the “younger granite” of Ohira (1982).

Mount Takamiyama consists of two types of rocks, namely, the Ryoke granite and the Takamiyama acidic rock (Umeda, 1973; Ohira,

1982). The Ryoke granite was formed at 80–90 Ma and was later mylonitized, on cooling, during the Upper Cretaceous at ~70 Ma (Shibata *et al.*, 1988). In the study area, closer to the MTL, the granite is mylonitized to a greater extent (Hara *et al.*, 1980; Ohira, 1982). Furthermore, the granitic body was intruded by Takamiyama acidic rocks during middle Miocene at ~12.8 Ma (Shibata *et al.*, 1988).

The granite ranges from adamellite to leucocratic grano-dioritic rocks, and is medium- to coarse-grained, weakly foliated and occasionally massive. The adamellite consists mainly of plagioclase, quartz, K-feldspar, biotite and opaques, with accessories of hornblende, zircon, tourmaline, allanite and rutile needles (Ohira, 1982). The Takamiyama acidic rocks are classified as granite porphyry and consist mainly of phenocrysts of K-feldspar, quartz, plagioclase and biotite in a matrix of K-feldspar, quartz, plagioclase, biotite and opaque minerals (Shibata *et al.*, 1988).

The granite is exposed along the ridge from east to west, almost parallel to the MTL. We collected two kinds of granites at similar distances from the MTL. One of the granites was sampled

at a considerable distance from the intrusive contact and the other was sampled at it (Fig. 1), representing mylonitized and recrystallized varieties, respectively. The granite samples collected were weakly weathered and contained dusty, milky plagioclases.

Recrystallized quartz

Under the optical microscope, naturally deformed quartz shows undulatory extinctions and is irregularly shaped with serrated grain boundaries. It can be seen that arrays of fine scale fluid inclusions cut across these grain boundaries, extending to other grains. However, quartz grains in the granite near the intrusive contact are fully recrystallized and sometimes have a polygonal shape with straight grain boundaries. The average grain size is $\sim 400 \mu\text{m}$. The recrystallized quartz is characterized by a smooth grain boundary, triple junction and flash extinction. Our observations suggest that the granitic rock has experienced no deformation due to the major movement of the MTL after recrystallization which was a result of the intrusion of the Takamiyama acidic rock. It can be assumed that the recrystallization occurred under static conditions.

Experimental

Doubly polished rock sections of the younger granite near the intrusive contact, which contains the recrystallized quartz, were prepared. Infrared spectra were obtained by FTIR (SHIMADZU FTIR-4200) spectrometry with optical microscopic instruments. All the measurements were performed with unpolarized IR light except for polarized IR measurement. A cooling-heating stage (LINKAM, TH-600PHS) was used to examine spectral change at various temperatures.

To examine the effect of irradiation on the sharp bands observed in the recrystallized quartz, we carried out X-ray irradiation and annealing experiments. X-ray irradiation was performed at conditions of 45 kV and 20 mA (Mo target) for 5 h duration at room temperature. The irradiated samples were annealed up to 450°C using the heating stage. Three IR spectra of the quartz were taken at -196°C of the same area before and after X-ray irradiation and also after annealing. We repeated these experiments four times to ensure reproducibility of the changes in spectra.

The samples were gradually heated up to temperatures of 600°C and cooled down to room

temperature during *in situ* high temperature measurements. Infrared spectra were obtained at each temperature.

Polarized-FTIR measurement requires an oriented single grain of the recrystallized quartz. Oriented thin sections cut parallel and normal to its *c*-axis were prepared. The grains of the recrystallized quartz were collected by hand-picking. Their crystallographic orientations were determined by an X-ray precession method. The quartz grains were mounted in resin and cut using a microcutter with a diamond saw and doubly polished with diamond paste. A polarized IR spectrum for an optically anisotropic crystal under the conditions of FTIR spectroscopy must take its optical characteristics into account and appropriate corrections should be applied (Shinoda and Aikawa, 1993, 1997). The least squares method was applied to curve fitting on calculation of polarization of OH dipole based on polarized-FTIR measurement results.

Results and discussions

Spectra of naturally deformed quartz and recrystallized quartz

Figure 2 shows typical IR spectra of the recrystallized quartz (lower) and that of naturally deformed quartz (upper) at room temperature. A

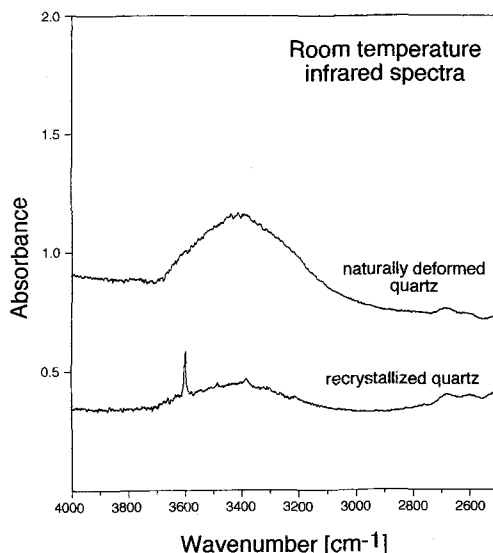


FIG. 2. Typical room temperature IR spectra of the naturally deformed quartz, 0.39 mm thick (upper), and of the recrystallized quartz, 0.61 mm thick (lower).

very sharp absorption band at 3596 cm^{-1} is observed in the recrystallized quartz. In some of the cases examined, a symmetric broad band centred at 3400 cm^{-1} is also observed. The spectrum of naturally deformed quartz does not show the 3596 cm^{-1} band at room temperature, and is characterized by a broad absorption band centred at 3400 cm^{-1} . From the spectra obtained, the absorption coefficient of the 3596 cm^{-1} band under unpolarized conditions at room temperature was calculated. The average is 2.10 abs. cm^{-1} with a variation of $\sim 20\%$.

Generally, as the background absorption is reduced at relatively low temperatures, the absorption bands between 3650 and 3200 cm^{-1} become very sharp and resolvable. Figure 3 shows the low temperature (-196°C) spectra of the recrystallized quartz (lower) and that of the deformed quartz (upper). Two other sharp bands at 3476 and 3369 cm^{-1} are also observed in the recrystallized quartz, whilst the deformed quartz shows no other sharp bands except for those at 3369 cm^{-1} and 3200 cm^{-1} . The absorption coefficient of the recrystallized quartz under unpolarized conditions at -196°C had an average of 3.01 abs. cm^{-1} .

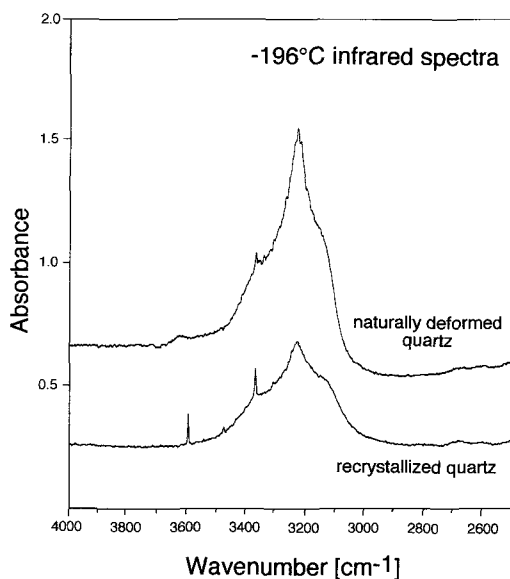


FIG. 3. Low temperature (-196°C) IR spectra of the naturally deformed quartz, 0.35 mm thick (upper) and of the recrystallized quartz, 0.38 mm thick (lower).

Irradiation effect

The continuous spectrum changes through X-ray irradiation and annealing experiments are shown in Fig. 4. The spectra were obtained at -196°C . The spectrum of the untreated recrystallized quartz shows sharp absorption bands at 3596 , 3476 , 3369 and 3308 cm^{-1} (Fig. 4 lower). After irradiation, the sharp absorption band at 3476 cm^{-1} disappeared (Fig. 4, middle), and the irradiated recrystallized quartz became smoky. On annealing up to 400°C , the 3476 cm^{-1} band reappeared (Fig. 4 upper) and the smoky coloured quartz was bleached to transparent. Throughout these experiments the 3596 cm^{-1} band does not show any detectable change in shape of spectrum, intensity or peak shift.

Pankrath (1991) examined the effect of γ -irradiation on the IR absorption bands of the synthetic crystal of smoky quartz at around 3400 cm^{-1} and showed that the 3596 cm^{-1} absorption band and other bands at around 3600 cm^{-1} disappeared after ^{60}Co - γ -irradiation. Niimi *et al.* (1995) examined the same recrystallized quartz as used in the present study and reported that the absorption band at 3476 cm^{-1} , associated with Li (Kats, 1962), disappeared at room temperature during X-ray irradiation with a

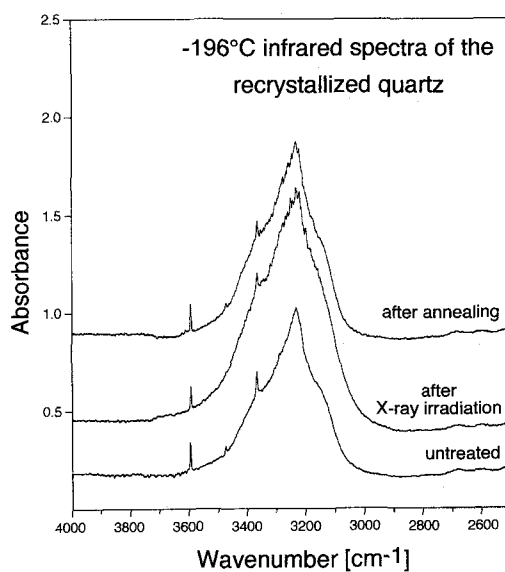


FIG. 4. Low temperature (-196°C) IR spectra of the untreated recrystallized quartz (lower), after X-ray irradiation (middle) and after annealing (upper). Sample thickness 0.45 mm .

Mo target, whilst the 3596 cm^{-1} band did not disappear and was not even diminished. The different behaviour at 3596 cm^{-1} in these two studies could be due to the nature of the radiation. Markes and Halliburton (1979) showed, by using an ESR technique that interstitial alkalis containing Na ions adjacent to Al which substitutes in quartz become mobile when the irradiation temperature is $>-73^\circ\text{C}$. Hydrogen in the form of OH became mobile even at -196°C irradiation. The band at 3476 cm^{-1} may be related to mobile alkali ions, whilst the 3596 cm^{-1} band is likely to be related to the H-related defect with no mobile alkalis.

High temperature behaviour

In situ high temperature spectra were obtained at various temperatures from room temperature to 600°C (Fig. 5). With increasing temperature, the 3596 cm^{-1} band diminishes in intensity, becoming broad and showing a peak shift towards a higher wavenumber. These changes are gradual. It is common in crystalline materials that OH bands tend to broaden upon heating (Aines and Rossman, 1985). The room temperature spectrum cooled from 600°C shows the band peaked at 3596 cm^{-1} again (Fig. 5 top). These results may be evidence for the stability of the 3596 cm^{-1} band at high temperatures. The 3596 cm^{-1} band also shows peak shift and broadening. The peak shift of the 3596 cm^{-1} band as a function of temperature is shown in Fig. 6. Although the shift value in wavenumber is very small, a positive shift against temperature is observed. The shift values of the peak position became ambiguous at temperatures $>400^\circ\text{C}$.

Polarized MFTIR measurement

Normalized absorbance (absorbance/cm) of the 3596 cm^{-1} band of the recrystallized quartz are plotted in the $(10\bar{1}0)$ (Fig. 7a) and (0001) planes of quartz (Fig. 7b). The sample cut parallel to the c -axis of quartz, including the a -axis, in the $(10\bar{1}0)$ plane, shows a pleochroism in absorbance distribution with a maximum of 1.82 perpendicular to the c -axis and minimum of 0.60 at the c -axis. However, the sample cut perpendicular to the c -axis shows an isotropic distribution in the (0001) plane. The calculation showed a highly polarized direction at the angle of $35.7^\circ (\pm 0.5^\circ, R: 0.975)$ from the a -axis towards the c -axis of quartz in the plane of $(10\bar{1}0)$.

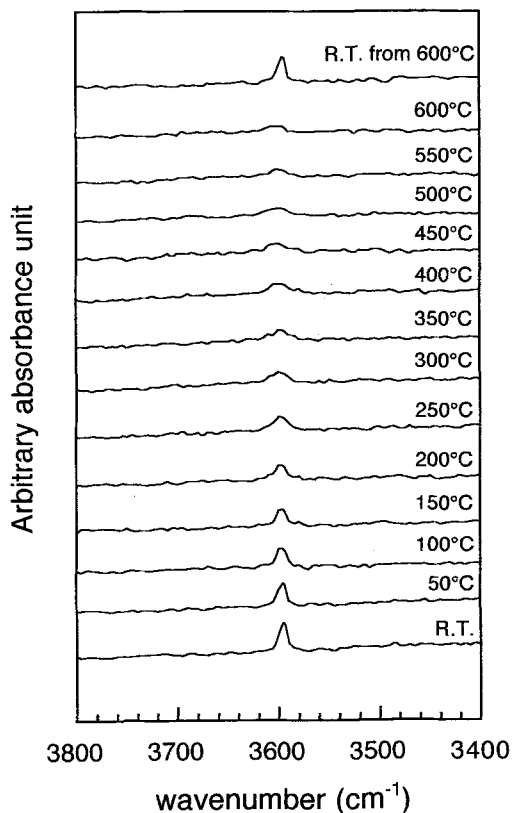


Fig. 5. Selected high temperature IR spectra of the recrystallized quartz in the range from room temperature to 600°C , showing intensity weakening and peak broadening. The top spectrum was obtained after cooling to room temperature from 600°C .

Comparison with other types of quartz

The recrystallized quartz in the present case shows a characteristically strong absorption band at 3596 cm^{-1} . An absorption band at 3596 cm^{-1} has been observed in amethyst (Chakraborty and Lehmann, 1976a,b; Rovetta *et al.*, 1989), clear Brazilian single crystals (Kronenberg *et al.*, 1986), chalcedony (Fron del, 1982), synthetic quartz crystals (Kats, 1962; Chakraborty and Lehmann, 1976a,b) and in synthetic smoky quartz (Pankrath, 1991). In these cases, the 3596 cm^{-1} bands were either very weak or faint. For comparison, normalized absorbance was used here because the band is relatively narrow. Normalized absorbance of the recrystallized quartz was calculated and compared with that of other types of quartz previously reported.

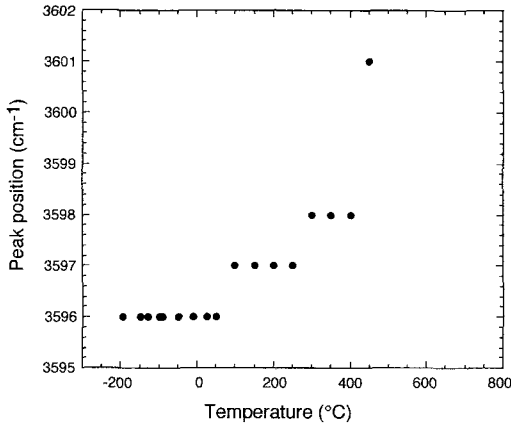


FIG. 6. Plot of the peak position of the 3596 cm⁻¹ band vs temperature, showing positive peak shift with increasing temperature.

Table 1 shows the absorption coefficient of the 3596 cm⁻¹ of various kinds of quartz. The absorption coefficients obtained for the recrystallized quartz are greater than any other values of other types of quartz. The absorption coefficients of synthetic quartz are particularly low.

Naturally deformed quartz studied here did not show the 3596 cm⁻¹ band even at the temperature of liquid nitrogen, showing only a symmetric broad band. This fact indicates that the major forms of H-related chemical species incorporated

into the recrystallized quartz and the deformed quartz are different: OH is a predominant form in the recrystallized quartz and H₂O aggregates as fluid inclusion in the deformed quartz.

Relationship of impurities with the 3596 cm⁻¹ band

Some absorption bands of quartz are closely related to a charge compensate type defect like Al coupled with alkalis (Kats, 1962). Figure 8 shows the plot of the trace elements of Li, Na, Al, K and Fe (atom/10⁶Si) in the quartz previously reported (Kats, 1962; Kronenberg *et al.*, 1986; Rovetta *et al.*, 1989; Pankrath, 1991) vs the absorbance of the 3596 cm⁻¹ band. Although there seems to be no correlation between the trace element content and the absorbance, all the samples have low Al contents. In many cases in the present study, the absorbance of the band varies to some extent from point to point even within a single grain of the recrystallized quartz. Great care must be taken in comparing the absorbance of the bands at individual points with impurity contents by bulk chemistry.

Possible assignment of the 3596 cm⁻¹ band

In spite of the large amount of previous work on the IR absorption bands of various kinds of quartz, the band at 3596 cm⁻¹ has not yet been assigned. The present results show the stability of the sharp 3596 cm⁻¹ band at temperatures of up

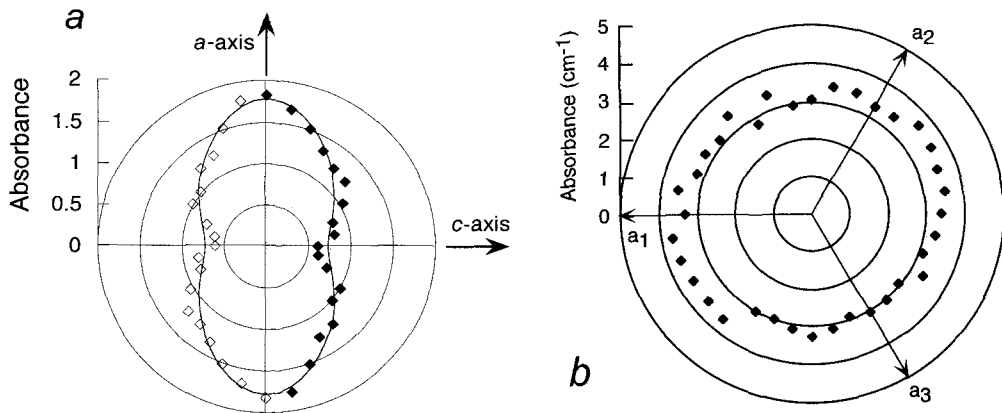


FIG. 7. (a) Distribution of polarized IR absorbance (normalized to abs. cm⁻¹) of the 3596 cm⁻¹ band in (1010) plane of the quartz. The *a*- and *c*-axes of the quartz are shown by arrows. The open symbols are plotted after symmetrical consideration. A best fitted calculated curve is also shown (solid line). The polarization of the band in (1010) plane is ~35.7° (±0.5°, R: 0.975). (b) Absorbance distribution in the (0001) plane of quartz is almost isotropic.

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TABLE 1. Normalized absorbance (abs. cm^{-1}) of the 3596 cm^{-1} band of the recrystallized quartz studied, and those of synthetic quartz, amethyst, natural clear quartz, and chalcedony

Specimens	abs. cm^{-1}	Reference
Synthetic quartz	<0.15	Pankrath, 1991 (77 K, $E \perp c$)
Synthetic quartz	<0.16	Kats, 1962 (77 K, $E \perp c$)
Mexican amethyst	0.26	Kats, 1962 (77 K, unpol.)
Italian amethyst*	<0.07	Kats, 1962 (77 K, $E \perp c$)
Italian amethyst**	0.84	Kats, 1962 (77 K, $E \perp c$)
Brazilian quartz [†]	<0.12	Kronenberg <i>et al.</i> , 1986 (77 K, unpol.)
Amethyst (Brazil)	<0.60	Rovetta <i>et al.</i> , 1989 (R.T., pol.)
Chalcedony	faint	Frondel, 1982
Recrystallized quartz [‡]	2.10	This study (R.T., unpol.)
Recrystallized quartz [‡]	3.01	This study (77 K, unpol.)
Recrystallized quartz	1.82	This study (R.T., $E \perp c$)
Recrystallized quartz	0.60	This study (R.T., $E \parallel C$)

* colourless part of Italian amethyst; ** violet part of Italian amethyst; [†] 3592 cm^{-1} ;
[‡] average of 17 grains. R.T. – room temperature; unpol. – unpolarized; pol. – polarized

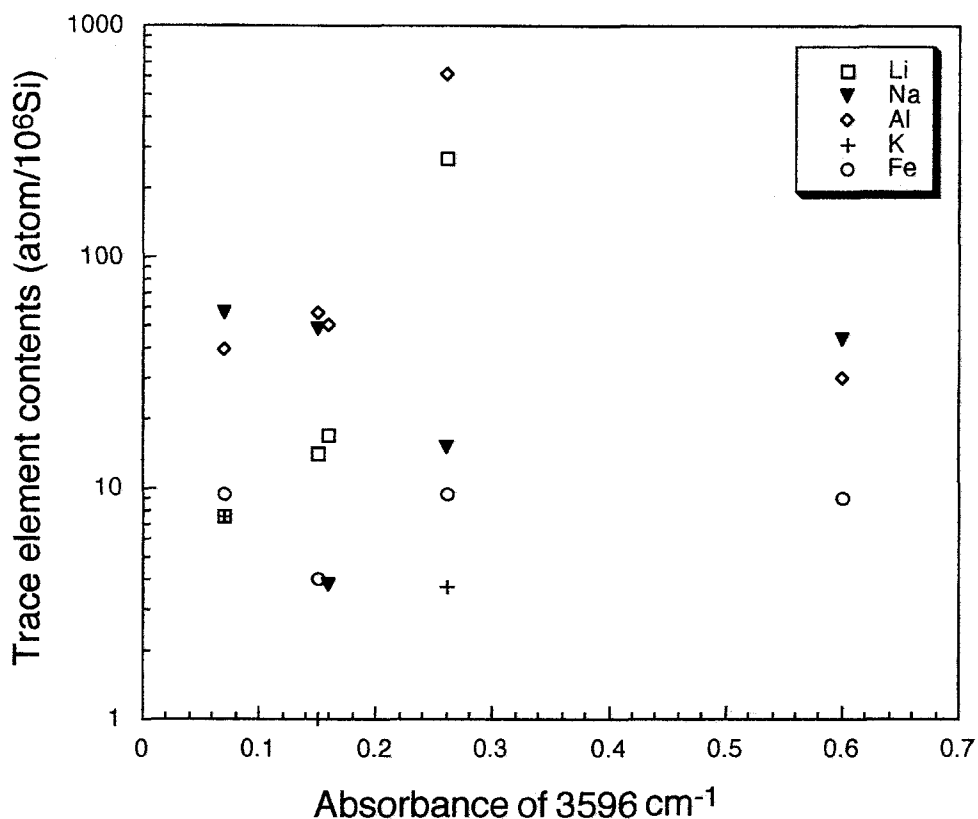


FIG. 8. Plot of absorbances of 3596 cm^{-1} band vs amounts of trace elements (atom/ 10^6Si). Data from Kats (1962), Kronenberg *et al.* (1986), Rovetta *et al.* (1989), Pankrath (1991).

to 600°C and during room temperature X-ray irradiation. Halliburton *et al.* (1981) revealed that in hydrogen-swept quartz, Al-OH centres are not affected by annealing above a temperature of 527°C. Aines and Rossman (1984) suggested that room temperature irradiation does not affect the Al(H) defect because the proton can diffuse back easily. Also, this Al(H) defect is most stable at high temperatures up to 1200°C at 1 atm, because they are an intrinsic part of the crystal structure (Aines and Rossman, 1984). These characters of the Al(H) defect are consistent with those obtained in the present study. It can be concluded that the 3596 cm⁻¹ band is due to the Al(H) type defect without alkalis which might occupy a structural position.

Conclusions

The Ryoke granite exposed at Mt. Takamiyama has experienced natural deformation before annealing by an intrusive rock. The recrystallized quartz in the granite always shows a very strong IR absorption band at 3596 cm⁻¹. The normalized absorbance of this band is 2.10 abs. cm⁻¹ at room temperature and 3.01 at 196°C under unpolarized conditions, 1.82 (*E* normal to the *c*-axis) and 0.60 (*E* parallel to the *c*-axis). These values are very large compared to those of other types of quartz reported previously, synthetic quartz, amethyst, Brazilian quartz, chalcedony and synthetic smoky quartz. Also, the 3596 cm⁻¹ band shows strong anisotropy in the (10 $\bar{1}$ 0) plane. By comparison with naturally deformed quartz, predominant forms of hydrogen-related species in the recrystallized quartz are considered to be different from those in naturally deformed quartz.

The stability of the sharp 3596 cm⁻¹ band during room-temperature X-ray irradiation and annealing at temperatures up to 600°C, its singularity in occurrence, and the lack of any correlation of the intensity of the 3596 cm⁻¹ band with impurities such as alkalis, suggest that it is the result of the Al(H) type defect without alkalis, which might occupy a structural position in the quartz structure.

Acknowledgements

The authors wish to express their appreciation to the members of mineralogy, petrology and geochemistry groups at O.C.U., for their constant encouragement. Thanks are due to Dr H.M. Rajesh for his help in improving in English text.

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[Manuscript received 14 September 1998:
revised 9 March 1999]