Absorption coefficients of overtone and combination modes of quartz

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Abstract

The *a*-, σ- and π-spectra of quartz in the IR regions were measured under FTIR spectroscopy, and overtone and combination modes perpendicular to the *c*-axis of quartz were confirmed to be electric vector active by the coincidence of the *a*-spectrum with the σ-spectrum among the three kinds of spectra. Absorption coefficients of overtone and combination modes intrinsic to the *a*-, σ-, and π-spectra of quartz were measured. The thickness of quartz thin sections can be determined by applying the absorption coefficients obtained from the *a*- and σ-spectra to the polarized IR absorption spectra measured under $E \perp$ the *c*-axis.

KEYWORDS: polarized absorbance spectrum, absorption coefficient, thickness determination, quartz.

Introduction

HYDROUS components in theoretically anhydrous minerals have significant effects on the physical properties of minerals. Hydrolytic weakening of quartz, for example, may be caused by minor amounts of hydrous components in quartz (Griggs and Blacic, 1965; Griggs, 1967; Kekulawala *et al.*, 1978; Doukhan and Trépied, 1985; Rovetta *et al.*, 1986; Cordier and Doukhan, 1989). Infrared absorption spectroscopy is one of the most useful methods to detect minor amounts of hydrous components in minerals (Aines and Rossman, 1984). Recently, Fourier transform infrared microspectroscopy (micro-FTIR) has been applied to the quantitative analysis of hydrous components in minerals with resolution of 10µm in diameter (MacMillan and Hofmeister, 1988). Kronenberg and Wolf (1990) carried out quantitative measurements of intragranular water contents of quartz and feldspar within various kinds of rocks by FTIR spectrometer. Nakashima *et al.* (1989) analysed the chemical state and spatial distribution of hydrous species in minerals under micro-FTIR.

Paterson (1982) suggested that the integral molar absorption coefficient of hydroxyl in silicates and glasses depends on the wavenumber, and proposed a liner calibration line of the integral molar absorption coefficient to determine the hydroxyl concentration in silicates and glasses. Measurement of the hydroxyl concentration of thin sections of quartz from IR absorption requires precise determination of thickness of the thin sections. Estimates of thickness based upon interference colors under crossed polars are not sufficient to determine the precise thickness of quartz thin sections and other methods are needed. Kronenberg and Wolf (1990) determined optical path lengths of quartz plates using Si-O absorption bands intrinsic to quartz at 267.3 mm^{-1} and 232.8 mm^{-1} However, the absorption coefficients of these two bands are too weak to determine the thickness of thin sections of several microns in thickness, and errors associated with dichroism of these absorptions may be as high as 3 and 10% respectively. Since grains of quartz in natural rocks are anhedral and randomly oriented, thickness determinations that do not depend on the orientation of quartz are necessary for the determination of the concentration of hydrous components in quartz. In the present study, an improved method to determine the thickness of arbitrarily oriented quartz is suggested by measuring absorption coefficients of overtone and combination modes between 210 and 140

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mm^{-1} intrinsic to the *a*-, *σ*-, and *π*-spectra of quartz under Fourier transform polarized infrared microspectroscopy (pol-mFTIR).

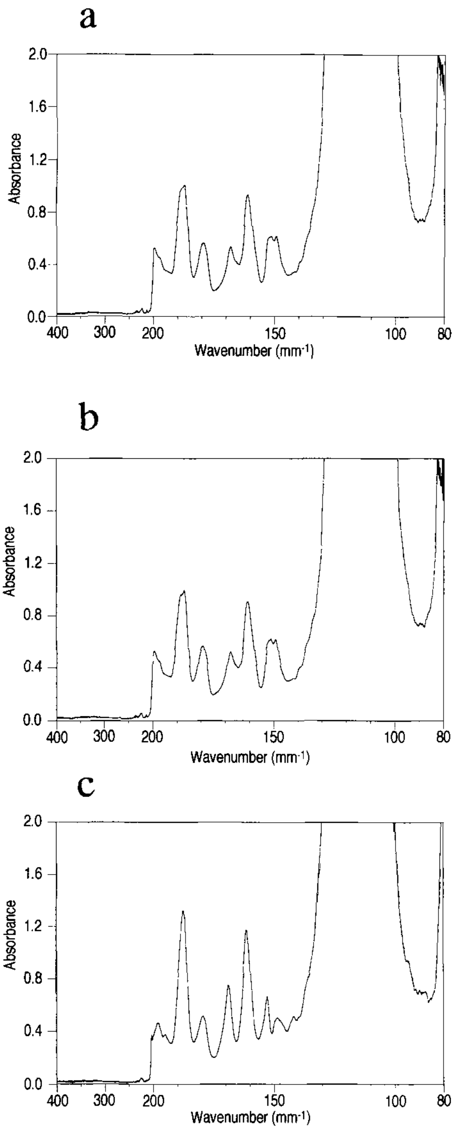

FIG. 1. Polarized IR absorption spectra of synthetic quartz. (*a*) *a*-spectrum with propagation vector of polarized IR light along the *c*-axis, (*b*) *σ*-spectrum with propagation vector and electric vector (*E*) of polarized IR light perpendicular to the *c*-axis, and (*c*) *π*-spectrum with propagation vector perpendicular to the *c*-axis and *E* parallel to the *c*-axis.

Experimental results

Shinoda and Aikawa (1993), have described in detail pol-mFTIR and its application to the measurement of polarized absorbance spectra, and requested to locate a thin section of an optically anisotropic crystal extinction position in order to avoid the interference fringes due to birefringence intrinsic to an optically anisotropic crystal. A pol-mFTIR system consisting of an FTIR spectrometer (Shimadzu FTIR4200) and an IR polarizing microscope (Shimadzu IMS-1) was used in this study, with vertical and lateral orientations on the sample stage labelled north-south (N-S) and east-west (E-W) following the convention of an optical microscope stage.

Fig.1 shows polarized IR absorbance spectra of synthetic quartz measured with the propagation vector of polarized IR light along the *c*-axis (Fig. 1*a*), with the propagation vector and electric vector (*E*) of polarized IR light perpendicular to the *c*-axis (Fig. 1*b*), and with the propagation vector perpendicular to the *c*-axis and *E* parallel to the *c*-axis (Fig. 1*c*). They are labelled *a*-, *σ*-, and *π*-spectra, respectively, after McClure (1959). The *a*-spectrum appears identical to the *σ*-spectrum (both with *E* perpendicular to *c*-axis) with absorption peaks observed at 199.8, 188.5, 187.1, 179.6, 168.1, 160.9, 151.3, and 149.4 mm^{-1}. In contrast, the *π*-spectrum (Fig. 1*c*) shows absorption peaks that differ from those of the *a*- and *σ*-spectra with bands located at 202.9, 197.9, 194.9, 187.3, 179.2, 168.7, 161.3, 152.7, and 148.5 mm^{-1}. All of these absorption peaks are considered to be due to overtone and combination modes intrinsic to quartz (Kats, 1962). As indicated in McClure (1959), the coincidence of *σ*- and *a*-spectra means that absorption peaks observed in the *a*-spectrum are due to electric vector active overtone and combination modes which are perpendicular to the *c*-axis. Therefore, the absorptions measured for $E \perp c$ are always identical to the spectrum in Fig.1*a* irrespective of the *c*-axis orientation. This prediction was confirmed experimentally by observing the spectrum for a synthetic quartz plate that was cut at 45° from the *c*-axis with $E \perp$ the *c*-axis. The absorptions observed in the *π*-spectrum are due to electric vector active overtone and combination modes that are parallel to the *c*-axis. Therefore, the absorptions in Fig.1*c* are produced only under $E \parallel$ the *c*-axis. Polarized IR absorbance spectra measured with *c*-axis inclined to *E* include components of both the *σ*- and *π*-spectra weighted by the angle between the *c*-axis and *E*.

Fig.2 shows the relations between thickness of quartz and absorbance for absorption peaks of *a*-

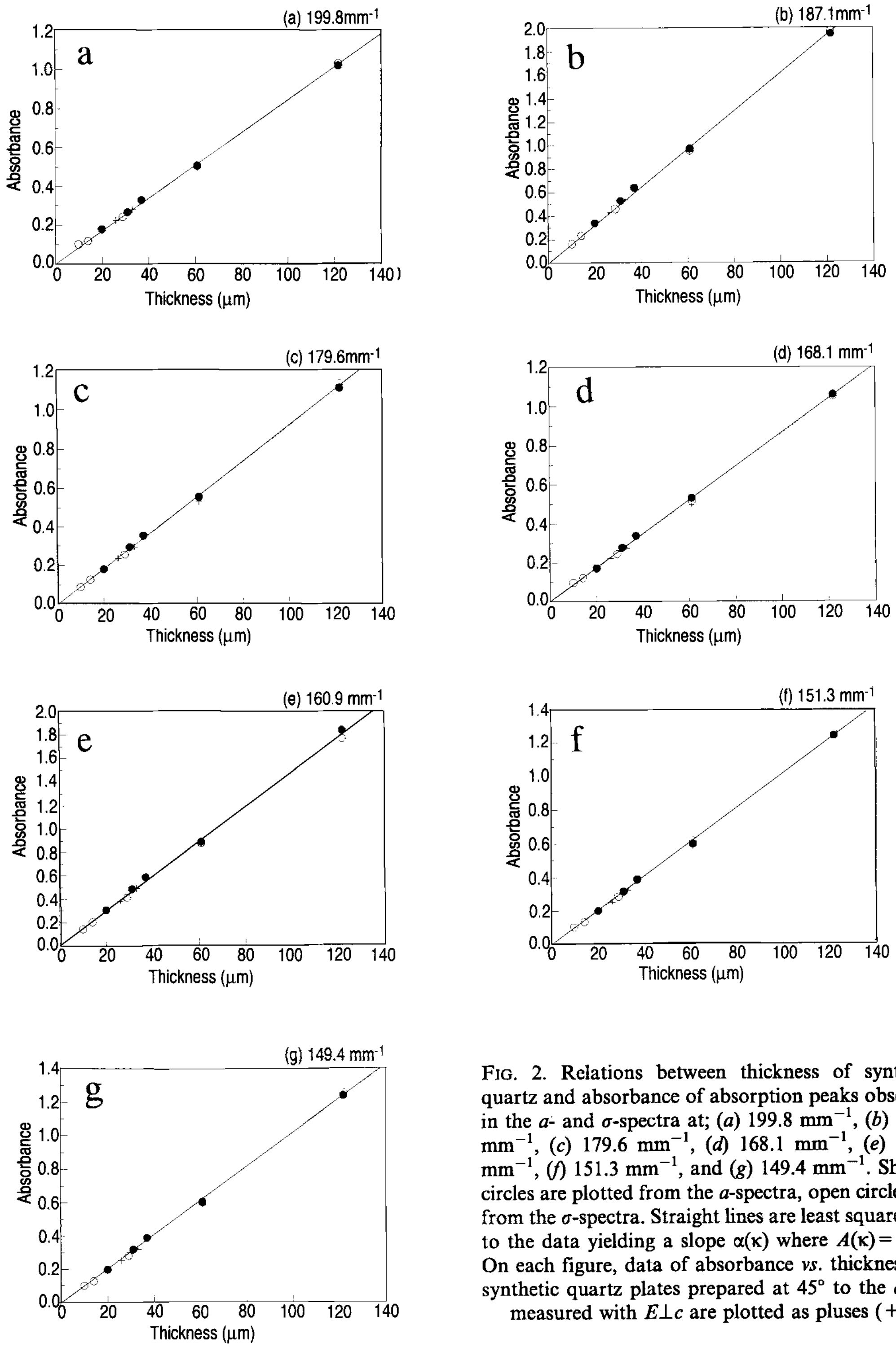

FIG. 2. Relations between thickness of synthetic quartz and absorbance of absorption peaks observed in the *a*- and *σ*-spectra at; (*a*) 199.8 mm^{-1}, (*b*) 187.1 mm^{-1}, (*c*) 179.6 mm^{-1}, (*d*) 168.1 mm^{-1}, (*e*) 160.9 mm^{-1}, (*f*) 151.3 mm^{-1}, and (*g*) 149.4 mm^{-1}. Shaded circles are plotted from the *a*-spectra, open circles are from the *σ*-spectra. Straight lines are least squares fits to the data yielding a slope $\alpha(\kappa)$ where $A(\kappa) = \alpha(\kappa)l$. On each figure, data of absorbance *vs*. thickness for synthetic quartz plates prepared at 45° to the *c*-axis measured with $E \perp c$ are plotted as pluses (+).

and σ-spectra at 199.8 mm^{-1} (*a*), 187.1 mm^{-1} (*b*), 179.6 mm^{-1} (*c*), 168.1 mm^{-1} (*d*), 160.9 mm^{-1} (*e*), 151.3 mm^{-1} (*f*), and 149.4 mm^{-1} (*g*). Thicknesses of quartz plates below 40 μm in thickness were determined by a channel spectrum method (Randall and Rawcliffe, 1967), where average refractive indices were measured directly under pol-mFTIR (Shinoda and Aikawa, 1993). The thickness of plates above 40 μm were determined by interference colours under crossed polars. Absorbances of each peak are proportional to optical path length by Lambert's Law $A(\kappa) = \alpha(\kappa)l$, where $A(\kappa)$ is absorbance, $\alpha(\kappa)$ is the absorption coefficient, l is the optical path length, and κ is wavenumber and least-squares fits yield values of absorption coefficients $\alpha(\kappa)$ for each absorption peak (Table 1). In the same way, absorption coefficients of overtone and combination modes for π-spectra were determined, as listed in Table 2.

Thickness determinations of quartz thin sections

The *c*-axis of quartz can readily be aligned perpendicular to *E* under the polarizing microscope. When a thin section of quartz of unknown orientation is set at its extinction position under IR microscope, which also completes the experimental request proposed by Shinoda and Aikawa (1993), either N-S or E-W is perpendicular to the *c*-axis, and the remaining direction is generally inclined to the *c*-axis. Among the two polarized absorbance spectra of quartz measured with $E \parallel$ NS and $E \parallel$ EW, one spectrum should be identical to Fig.1*a* and can be identified as $E \perp c$ with absorption bands of the σ-spectrum. Once *E* has been oriented perpendicular to *c*, the thickness of quartz can be practically determined using the absorption coefficients of the σ-spectrum. As a check of this method, thin sections of synthetic quartz were cut at 45° to the *c*-axis (plotted as pluses (+) Fig. 2*a*-*g*). The absorbances obtained for these samples were measured with $E \perp c$ and are in good agreement with the best-fit line for *a*- and σ-spectra. Therefore, absorption coefficients of overtone and combination modes intrinsic to the *a*- and σ-spectra of quartz can be used for the determination of thickness of quartz thin sections of the order of micrometres in thickness.

The thickness of a quartz thin section can also be determined by an unpolarized absorption spectrum of quartz. The unpolarized absorption spectrum of an arbitrarily oriented quartz thin section is the combination of σ- and π-spectra, and the combining ratio of the two spectra depends on the angle between the *c*-axis and the propagation vector of the IR light. Both σ- and π-spectra include absorption peaks around 152.0 mm^{-1} with absorption coefficients of about 10 mm^{-1}. Using an average absorption coefficient of 10.4 mm^{-1}, the thickness of a quartz thin section; l (mm) can be practically determined from the absorbance; A at 152.0 mm^{-1} of the unpolarized absorption spectra with errors of about 2%.

Application to water content determinations of naturally deformed quartz in mylonites

The thickness determination method proposed was applied to determine water contents of naturally deformed quartz in mylonites of the Deai district, Nara Prefecture, Japan. Granitic rocks in the Deai district were deformed by tectonic movement along the Median Tectonic Line (M.T.L.) over a width of 4km in the northern area of the M.T.L.. Ductile deformation features (undulose extinction, deformation lamellae and recrystallization) of quartz become marked towards the center of the M.T.L. (e.g. Takagi,

TABLE 1. Absorption coefficients of absorption peaks from the *a*- and σ- spectra

Wavenumber (mm^{-1})	Absorption coefficient (mm^{-1})
199.8	8.41 (±0.05)
187.1	16.09 (±0.11)
179.6	9.16 (±0.05)
168.1	8.66 (±0.04)
160.9	14.80 (±0.12)
151.3	10.18 (±0.05)
149.4	10.15 (±0.06)

TABLE 2. Absorption coefficients of absorption peaks from the π-spectrum

Wavenumber (mm^{-1})	Absorption coefficient (mm^{-1})
202.9	5.92 (±0.04)
197.9	7.51 (±0.07)
194.9	6.03 (±0.07)
187.3	21.11 (±0.15)
179.2	8.23 (±0.05)
168.7	12.16 (±0.05)
161.3	18.36 (±0.08)
152.7	10.68 (±0.09)
148.5	8.19 (±0.13)

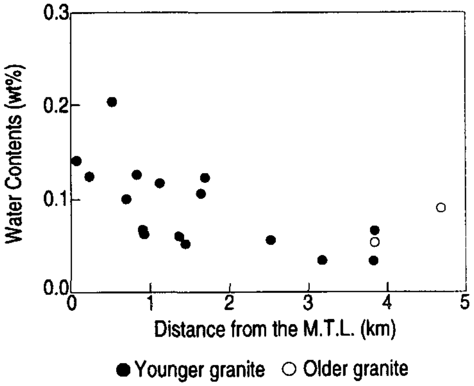

FIG. 3. Water contents of quartz in mylonite from the Median Tectonic Line (M.T.L.) at Deai district, Nara Prefecture, Japan.

1986, Hara *et al.* 1980). Quartz in granitic rocks collected as a function of distance from the M.T.L. were examined under the pol-mFTIR, and water contents were determined from absorbances due to OH stretching modes as proposed in Aines and Rossmann (1984). The results obtained are shown in Fig. 3. Water contents of deformed quartz grains decrease with increasing distance from the M.T.L.. Change in the lattice microstrain of deformed quartz associated with the strain fields around dislocations were estimated from line broadening of powder X-ray diffraction peaks of pulverized quartz specimen. Using this measure of deformation, lattice microstrains in quartz decrease with increasing distance from the M.T.L. with a similar trend as observed for water contents. Thus, hydrous components may have played an important role in the deformation of quartz in nature. The role of the hydrous component in the deformation process will be discussed in the separate paper (Shinoda *et al.*, in preparation).

Conclusion

The infrared a-, σ-, and π-spectra of quartz were measured by FTIR spectroscopy. The close comparison of the a-spectrum with the σ-spectrum indicates that the overtone and combination modes perpendicular to the c-axis of quartz are electric vector (E) active, and suggests that polarized IR absorbance spectra for samples of arbitrary orientation measured with $E \perp c$ exhibit absorptions identical to the a- and σ-spectra. The c-axis of quartz grains in thin section can always be oriented perpendicular to (E) under pol-mFTIR. Absorption coefficients of overtone and combination modes between 210 and 140 mm^{-1} intrinsic to the a- and σ-spectra and the π-spectrum of quartz were measured. Thus the thickness of quartz grains in thin sections of quartz-bearing rocks can be determined by the absorption coefficients of the a- and π-spectra.

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References

Aines, R. D. and Rossman, G. R. (1984) Water in minerals? A peak in the infrared. *J. Geophys. Res.*, **89**, 4059–71.

Cordier P. and Doukhan, J. C. (1989) Water solubility in quartz and its influence on ductility. *Eur. J. Mineral.*, **1**, 221–37.

Doukhan, P. and Trépied, L. (1985) Plastic deformation of quartz single crystals. *Bull. Minéral.*, **108**, 97–123.

Griggs, D. T. (1967) Hydrolytic weakening of quartz and other silicates. *Geophys. J.*, **14**, 19–32.

Griggs, D. T. and Blacic, J. D. (1965) Quartz: anomalous weakness of synthetic crystals. *Science*, **147**, 292–5.

Hara, I., Shyoji, K., Sakurai, Y., Yokoyama, S. and Hide, K. (1980) Origin of the Median Tectonic Line and its initial shape. *Memoir. Geol. Soc. Japan*, **18**, 27–49.

Kats, A. (1962) Hydrogen in alpha quartz. *Phillips Res. Repts.*, **17**, 133–95,201–79.

Kekulawala, K. R. S. S., Paterson, M. S. and Boland, J. N. (1978) Hydrolytic weakening in quartz. *Tectonophysics*, **46**, T1–T6.

Kronenberg, A. K. and Wolf, G. H. (1990) Fourier transform infrared spectroscopy determinations of intragranular water content in quartz-bearing rocks; Implications for hydrolytic weakening in the laboratory and within the earth. *Tectonophysics*, **172**, 255–71.

MacMillan, P. F. and Hofmeister, A. M. (1988) Infrared and Raman spectroscopy. Spectroscopic methods in mineralogy and geology. In: *Reviews in Mineralogy* (Hawthorne, F. C., ed.) Mineralogical Society of America, **18**, pp. 99–159.

McClure, D. S. (1959) Electronic spectra of molecules in crystals. Part II. Spectra of ions in crystals. In: *Solid State Physics.* (Seitz, f. and Turnbull, D., eds.) Academic press INC., London. 9, pp. 400–525.

Nakashima, S., Ohki, S. and Ochiai, S. (1989) Infrared spectroscopy analysis of the chemical state and the spatial distribution of hydrous species in minerals. *Geochem. J.*, **23**, 57–64.

Paterson, M. S. (1982) The determination of hydroxyl by infrared absorption in quartz, silicate glasses and similar materials. *Bull. Mineral.*, **105**, 20–29.

Randall, C. M. and Rawcliffe, R. D. (1967) Refractive indices of germanium, silicon, and fused quartz in the far infrared. *Appl. Opt.*, **6**, 1889–95.

Rovetta, M. R., Holloway, J. R. and Blacic, J. D. (1986) Solubility of hydroxyl in natural quartz annealed in water at 900°C and 1.5 GPa. *Geophys. Res. Lett.*, **13**, 145–8.

Shinoda, K. and Aikawa, N. (1993) Polarized infrared absorbance spectra of an optically anisotropic crystal: Application to the orientation of the OH^- dipole in quartz. *Phys. Chem. Minerals*, **20**, 308–14.

Takagi, H. (1986) Implication of mylonitic microstructures for the geotectonic evolution the Median Tectonic Line, central Japan. *J. Struct. Geol.*, **8**, 3–14.

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