Water speciation in quartz: A near infrared study

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Abstract

Water speciation in quartz has been investigated by infrared and near-infrared spectroscopy and by transmission electron microscopy (TEM). Water-related point defects cannot be distinguished from as-grown tiny aggregates of molecular water by infrared spectroscopy, except if water occurs in the form of bubbles large enough for water to be a fluid phase. In very "wet" quartz (a few hundred atomic ppm or more), water molecules in aggregates represent the prominent species. We show that water can also be incorporated in the form of a supersaturated solution of point defects with a concentration as high as 180 atomic ppm in some synthetic samples. In the case of a solution of water point defects, the near infrared absorbance spectra are expected to exhibit a pleochroism, which has been evidenced using polarized light. However, it has not been possible to fully characterize the structure of these water-associated point defects because of the low absorbance in this spectral range.

Introduction

Water[1] has been known for many years to dramatically affect the plastic behavior of quartz. Numerous experimental studies of plastic deformation of "wet" quartz[2] have been carried out since the discovery of hydrolytic weakening by Griggs and Blacic (1965). They can be summarized in the following way: water-free (i.e., "dry") single crystals (natural as well as premium quality synthetic crystals) fracture in the brittle regime at very high stress, even at temperatures as high as $0.8\ T_m$ (T_m is the melting temperature in K). In contrast, "wet" crystals deform easily (compressive stress of a few hundred MPa) at only 400 °C (see a review of deformation experiments on "wet" quartz in Doukhan and Trépied, 1985). Recent studies have shown that the mechanisms responsible for this weakening depend on the speciation of water in quartz. If water is supersaturated under the deformation conditions, precipitation will occur, dislocation multiplication will be enhanced, and dislocation climb will be promoted (McLaren et al., 1989; Cordier and Doukhan, 1989). These processes may result in drastic weakening of crystals. If, on the contrary, the water species remain in the quartz structure, only glide of dislocations is promoted (Cordier and Doukhan, 1989). The crystal becomes ductile but remains fairly strong and exhibits significant strain hardening.

The way in which water is incorporated into quartz now seems to be the key to understanding the basic mechanisms of hydrolytic weakening of quartz. Is water incorporated as a fluid phase dispersed in tiny bubbles, does it occur in quartz as isolated, randomly distributed point defects? In the latter case, what kind of defects are involved? Molecular water can be incorporated into quartz into the form of fluid inclusions. Fluid inclusions are usually detected by optical microscopy in both natural and synthetic quartz (they are generally most readily observed near the seed in the latter case). Such fluid inclusions are not thought to play an important role in plastic deformation, as they are dispersed at a macroscopic scale. Water can also be incorporated in tiny bubbles (as small as 30 Å) dispersed in the matrix (Cordier et al., 1988). They can only be imaged by using transmission electron microscopy (TEM).

The most common tool used to study water in quartz (and, more generally, in minerals) is infrared (IR) spectroscopy (see, for instance, Kats, 1962; Aines and Rossman, 1984). The infrared radiation is absorbed by the O-H bonds in the so-called 3-μm band (i.e., between 4000 and 2500 cm^{-1}). Stretching and bending modes of the O-H bonds are responsible for this absorption. The total water content of a given crystal can be determined using this technique by measuring the integral absorbance between 4000 cm^{-1} and 2500 cm^{-1} (Paterson, 1982). The infrared absorbance of "wet" quartz is composed of a broad band extending approximately from 3600 to 2500 cm^{-1}, with a number of sharp absorption peaks superimposed on it. Some of these peaks have been attributed to H-compensated impurities (Kats, 1962), whereas the origin of the broad band remains unclear. A limitation of

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[1] The term "water" is used for any species with O-H bonds detected through IR absorption in the 3-μm band (e.g., OH or H_2O). Only when H_2O or water molecules can be specified are they referred to as such in this paper.

[2] The term "wet" is used to describe quartz containing O-H bonds detectable by IR spectroscopy.

IR spectroscopy is that it provides little information regarding the defects responsible for this absorption. A more powerful technique is near-infrared (NIR) spectroscopy in the range 7000–4500 cm⁻¹, which allows molecular water and point defects to be distinguished. This method has been successfully applied to the study of glasses (Bartholomew et al., 1980; Stone and Walrafen, 1982; Stolper, 1982) and various forms of silica (Langer and Flörke, 1974; Flörke et al., 1982) including quartz (Aines and Rossman, 1984; Aines et al., 1984). The full list of peak assignments is included in the above references. From a practical point of view, two NIR absorption bands are of particular interest: the one at 4500 cm⁻¹, which results only from the vibration modes of isolated OH point defects (i.e., of Si-OH groups), and the one at 5200 cm⁻¹, resulting from a combination of the bending and stretching vibration modes of H_2O molecules. It is thus possible from the examination of a NIR spectrum to differentiate molecular water from point defects.

The nature of the water point defects is still controversial, and a number of defect models have been proposed. Nutall and Weil (1980) and Weil (1984) have characterized, by electron spin resonance (ESR), the substitutional defect $(4H)_{Si}$ that is formally equivalent to the substitution for SiO_2 of two H_2O. Other models of point defects cited in the literature include interstitial water molecules in the channels parallel to the c-axis (Hagon et al., 1987) and hydrolyzed Si-O-Si bonds, i.e., water molecules having chemically reacted with quartz leading to Si-OH–OH-Si [this is the first model of water incorporation proposed by Griggs (1967)]. H-like alkali ions can be associated with substitutional impurities (such as Al^{3+} or Fe^{3+}) to maintain charge balance. The existence of the $Al-OH^-$ defect has been well established by ESR and IR spectroscopy (3306 and 3367 cm⁻¹ absorption bands) by Halliburton et al. (1981). Nevertheless it is unlikely that this kind of defect plays an important role in hydrolytic weakening, as its diffusivity is expected to be low. In the following discussion, we will not consider defects such as water molecules physically or chemically sorbed on free surfaces (external surfaces or cracks) nor water associated with defects such as dislocations or grain boundaries. Only single crystals will be considered here.

The study described here deals with NIR characterization of "wet" quartz single crystals and tentative determination of the structure of water-related point defects.

EXPERIMENTAL TECHNIQUES

Specimens

We have analyzed a number of crystals by IR and NIR spectroscopy. Some have been grown by the General Electric Company (GEC Wembley, U.K.) in nutrients deliberately used to obtain doped quartz. (These crystals have been kindly provided by V. Cheel and D. H. Mainprice.) As shown below, the dominant impurity in these crystals is water. Another crystal that has been extensively used for various types of experiments in our laboratory

was grown 20 years ago by Bell Telephone Company (crystal kindly provided by A. C. Chaklader, University of British Columbia, Vancouver, Canada). All others have been grown by the Société Industrielle de Combustible Nucléaire (SICN Annecy, France) in the usual growth conditions (170 MPa, 350–370 °C, molar solution of NaOH as nutrient). The one crystal labeled L was grown with a high growth rate (approximately 0.5 mm/d) in a small autoclave (10 L). Others labeled 229 and 140 were grown in the large autoclaves used for production (growth rate on the order of 0.3 mm/d).

Infrared and near-infrared spectroscopy

All of the conventional IR spectra have been recorded with a 882 Perkin-Elmer spectrometer using unpolarized light at room temperature and in air. The double beam of the spectrometer eliminates the perturbations caused by H_2O vapor in air. The chosen resolution was 2.4 cm⁻¹.

The NIR spectra (wavenumber range 5500–4000 cm⁻¹) have been recorded in air at room temperature, with a spectrometer built in our laboratory. This spectrometer has only one beam; therefore, a blank spectrum (without sample) must be recorded for calibration before each experiment. Two detectors measure, for each wavenumber, the incident and the transmitted intensities (i.e., before and after the sample measurement). Most of the experiments have been performed with unpolarized light, but for experiments requiring polarized light, a Cambridge IGP 228 polarizer was used. The resolution of the spectrometer varies with the wavelength, from 15 cm⁻¹ for the largest wavenumber (5500 cm⁻¹) to 35 cm⁻¹ for the lowest (4000 cm⁻¹). Recording a NIR spectrum with the above conditions requires approximately 2 h. Furthermore, for most of the samples, we have also recorded another spectrum with a higher resolution (18–25 cm⁻¹) in the range 4760–4255 cm⁻¹, which corresponds to the absorption band for the point defects. Under these conditions the recording time reaches 4 h. Because of the very low absorbance in the NIR spectral region, 200 measurements were accumulated for each wavenumber in order to increase the signal to noise ratio; further noise reduction was obtained by eliminating the high frequencies of the Fourier transforms of the spectra. Comparison of the OH content of the various samples requires precise spectra in the range 4760–4255 cm⁻¹; the base line caused by interference by other peaks has thus been subtracted. Finally, the absorption band for the point defects has been tentatively decomposed to a series of sharp peaks with Gaussian profiles. This deconvolution operation has been performed with the help of a top-hat numerical filter (McCarthy and Schambers, 1981).

WATER IN QUARTZ: POINT DEFECTS OR WATER MOLECULES?

As noted above, it is essential to determine if water is aggregated in tiny bubbles or if it truly exists in the quartz structure in the form of point defects (with an unelucidated structure). Contrasting modes of plastic deformation (deformation controlled by dislocation climb or dis-
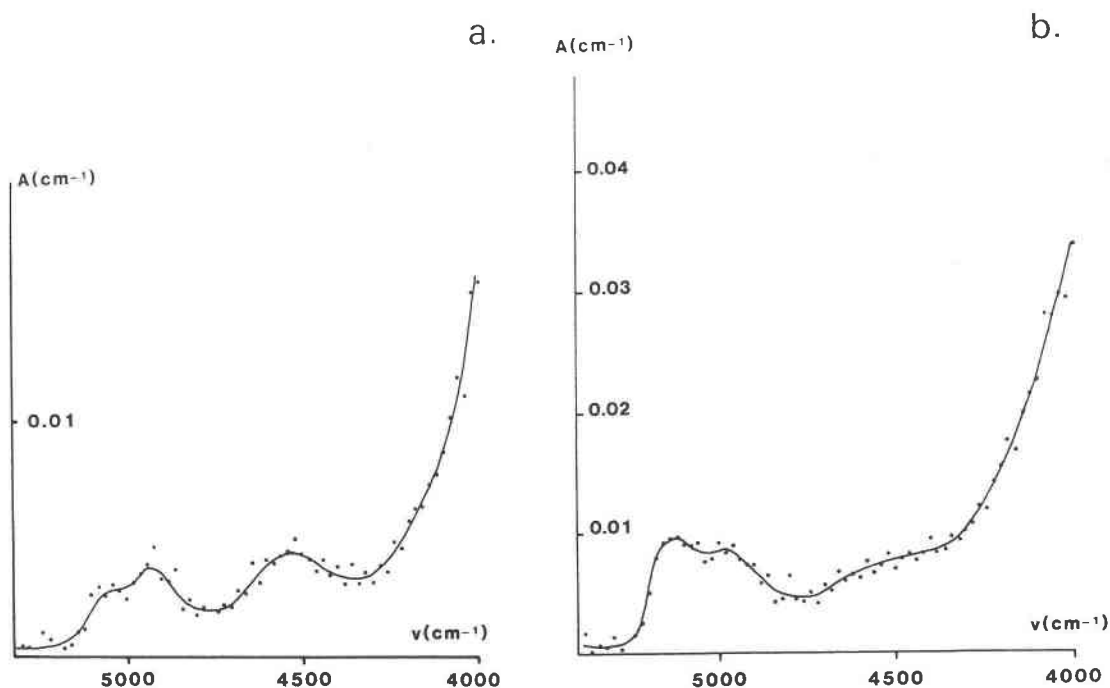
Fig. 1. Two NIR spectra of the Bell Telephone crystal recorded (a) at the end of growth, water content 150 atomic ppm; (b) in the middle of the crystal, water content = 600 atomic ppm; thickness = 2.5 cm (A stands for "absorbance").

location glide, respectively) result from these two different modes of water incorporation.

Figure 1 shows NIR spectra of the Bell Telephone crystal from two regions of the specimen. The crystal is a "wet" but otherwise pure material; its total water content (determined by conventional IR spectroscopy) varies from H/Si = 1000 atomic ppm, in the vicinity of the seed of the crystal, down to 150 atomic ppm, near the surface. The corresponding NIR spectra indicate that, near the seed, only molecular water occurs. In contrast, far from the seed, both types of OH occur, the amount of molecular water is lower, and the absorption band for the point defects becomes clearly visible. Figure 2 is a TEM micrograph corresponding to this material. There are numerous features exhibiting strain contrast that are characteristic of hydrostatic pressure centers. In this crystal, molecular water is incorporated in overpressurized tiny bubbles (perhaps described as aggregates). Similar observations have been previously reported for other synthetic quartz samples (Morrison-Smith et al., 1976; Kekulawala et al., 1981; Gerretsen et al., 1989).

The crystals grown in deliberately doped nutrients contain water. Their IR spectra indicate a H/Si ratio of 500, 2400, and 1400 atomic ppm, respectively, for the P-, Al-, and Ti-doped specimens [concentrations determined with the calibration proposed by Paterson (1982)]. Their NIR spectra show only molecular water except for the Al-doped crystal, which also contains water point defects (Fig. 3). TEM investigations confirm the presence of numerous tiny bubbles in all of these crystals (illustrated in Fig. 4 for the case of the Ti-doped crystal). However in

these crystals, the water aggregates do not seem to show strain contrast indicative of high hydrostatic pressure. In fact, even when the nutrient was heavily doped with P, Al, or Ti, the main impurity which was detected in the crystals was water. A tentative explanation is that during hydrothermal growth, the impurities influence the degree of polymerization of silica in the nutrient. Very long, hy-
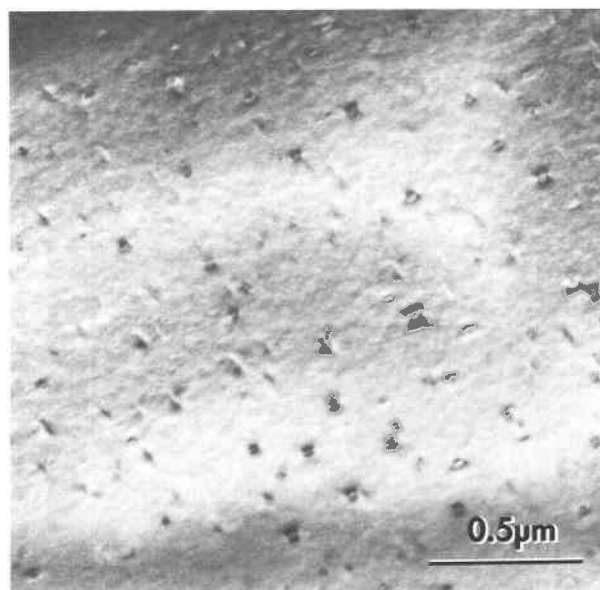

Fig. 2. TEM micrograph corresponding to the region of Figure 1b containing 600 atomic ppm; $g = 10\bar{1}1$; bright field.
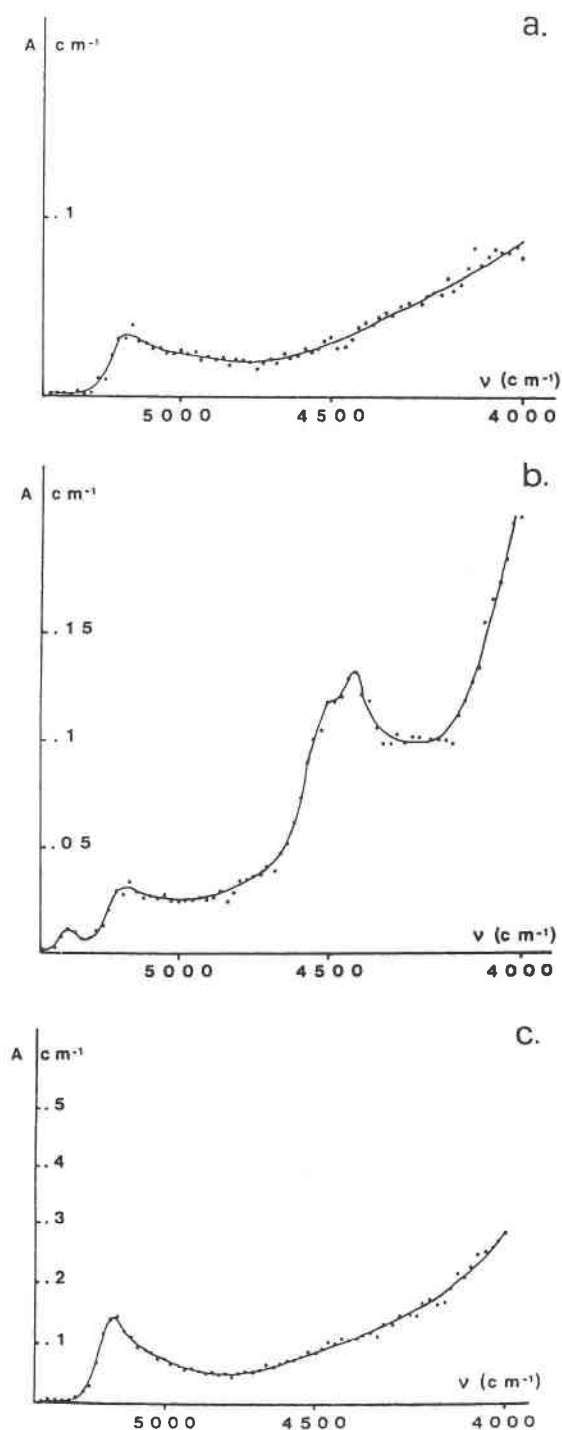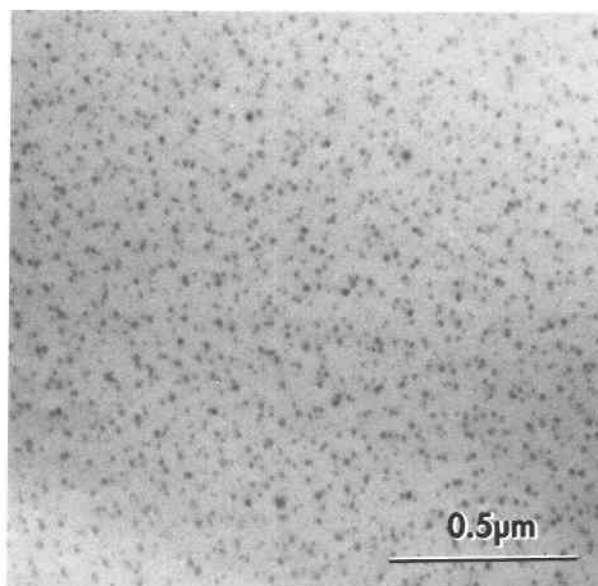
a.

b.

Fig. 4. Ti-doped crystal; TEM micrograph showing the tiny bubbles; $\mathbf{g} = 10\bar{1}1$; bright field.

c.

this case, many point defects are incorporated that probably are charge compensated by OH. Crystals with such defects compare to natural amethyst (NIR absorption in Fig. 5). Such crystals can have a high water content and contain Al as an impurity.

The SICN crystal labeled L, which was synthesized at a high growth rate, is "wet." It has a rather homogeneous water content; H/Si ≈ 1000 atomic ppm, and the crystal contains only molecular water (Fig. 6).

The other SICN crystals, labeled 140 and 229, are of major interest because they contain only water point defects in the amounts of 180 and 100 atomic ppm, respectively (Fig. 7). An interesting point is that this concentration of point defects corresponds to supersaturation
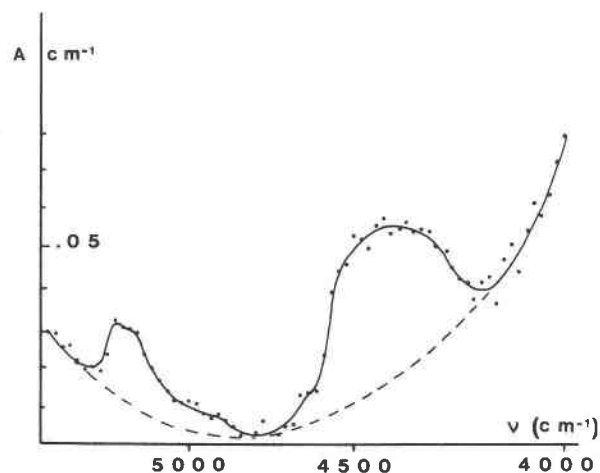
Fig. 3. NIR spectra of synthetic crystals grown in doped nutrients: (a) dopant = P; water content ≈ 500 atomic ppm; thickness = 0.62 cm; (b) dopant = Al; water content = 2400 atomic ppm; thickness = 0.6 cm; (c) dopant = Ti; water content = 1400 atomic ppm; thickness = 0.52 cm.

Fig. 5. NIR spectrum of a natural amethyst specimen; thickness = 0.8 cm.

drated chains could be incorporated in the growing crystal. Subsequently, water molecules or OH ions could reorganize in tiny fluid inclusions with a low inner pressure. A special role seems to be played by the dopant Al. In
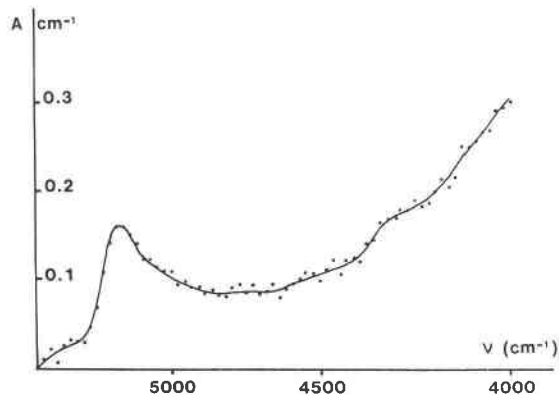
Fig. 6. NIR spectrum of SICN L crystal; thickness = 0.38 cm.

even for the growth conditions. The concentration 100 atomic ppm corresponds to the solubility at 700 °C, 800 MPa (Cordier and Doukhan, 1989), whereas typical growth conditions of synthetic crystals are 350–370 °C, 170 MPa.

These results show that if a synthetic quartz crystal is "wet" (a few hundred atomic ppm or more) "water" will be present largely as molecular water in high-pressure aggregates. Those aggregates can be detected by NIR spectroscopy and by TEM. This remains true if the crystal is not pure, except for Al-doped crystals, because the Al impurity allows the dissolution of large amounts of OH in the form of Al-OH defects. For crystals with a lower water content (H/Si ≈ 100 atomic ppm) and for some growth conditions, a supersaturated concentration of point defects can be incorporated. We know that these point defects induce the NIR absorption band centered on 4500 cm⁻¹ and enhance dislocation glide (Cordier and Doukhan, 1989). Finally, we point out that two synthetic crystals, Bell Telephone and SICN 140, with completely

different modes of water incorporation (water aggregates and point defects, respectively) exhibit similar conventional IR spectra (Fig. 8). The asymmetric broad band cannot be regarded as an unambiguous signature of a well-defined microstructure for H_2O or OH.

EVOLUTION DURING ANNEALING

The mechanisms of water precipitation and coalescence have been studied in detail in quartz (Cordier et al., 1988; Gerretsen et al., 1989). Given the original microstructure (point defects or tiny bubbles), its evolution during annealing at room pressure is well characterized. Study of infrared spectra obtained during annealing of "wet" quartz should therefore be fruitful.

The influence of annealing at atmospheric pressure on the IR spectrum is shown in Figure 9 for the Bell Telephone Company crystal (sample cut from a region containing 200 atomic ppm with both point defects and molecular water). There is an increase in height of some absorption peaks (e.g., at 3580 and 3430 cm⁻¹), whereas the absorbance decreases in the region between 3400 and 2900 cm⁻¹. A similar evolution is observed for the "wet" quartz sample SICN 229, which initially contains only water-related point defects (Fig. 10). The evolution is also similar for annealing experiments at moderate pressure (<500 MPa). NIR spectra for the SICN 140 crystal annealed at atmospheric pressure clearly show a decrease in the height of the absorption band corresponding to point defects, whereas that of the band corresponding to molecular water increases (Fig. 11).

The increase in height of the sharp absorption peak at 3580 cm⁻¹ after annealing has already been reported by Rovetta et al. (1986) for samples hydrothermally annealed at 900–1000 °C, 1000–1200 MPa. These authors attributed this effect to water trapped in microcracks. This conclusion cannot be correct for the annealing at room
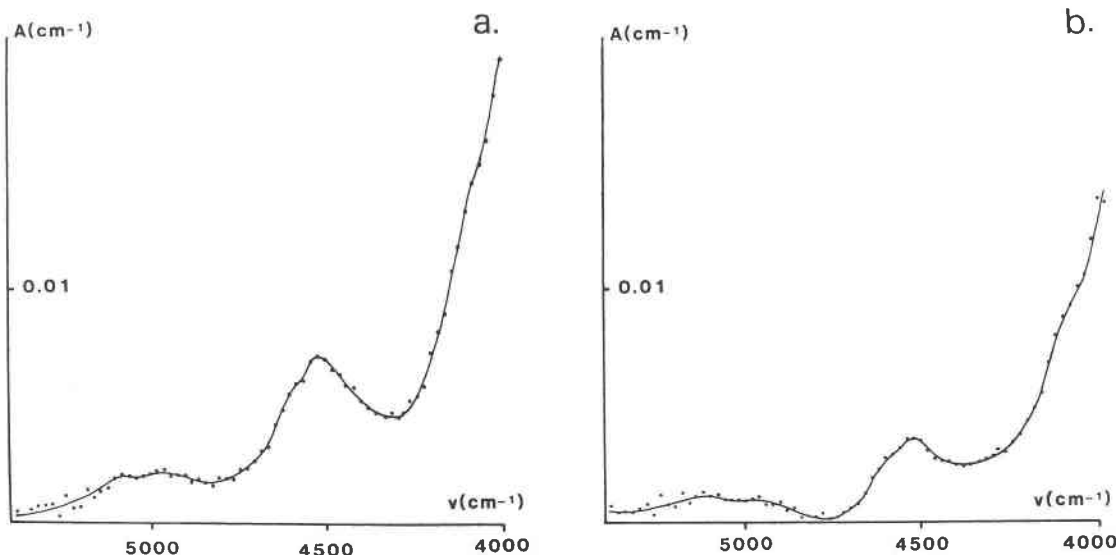

Fig. 7. NIR spectra of synthetic SICN crystals. (a) SICN 140; water content = 180 atomic ppm; thickness = 9 cm; (b) SICN 229; water content = 100 atomic ppm; thickness = 13 cm.
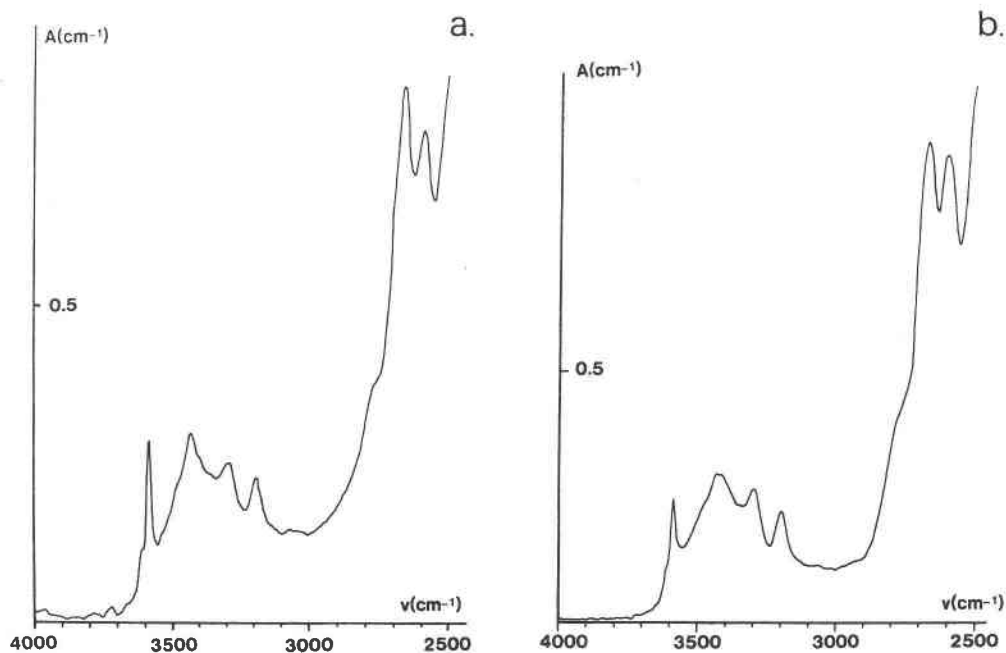
Fig. 8. IR spectra of two synthetic crystals. (a) Bell Telephone crystal containing mainly water molecules in high-pressure aggregates. (b) SICN 140 containing point defects in solution. No significant differences can be observed in these conventional IR spectra.

pressure reported in this study, for which microcracking was carefully avoided. This peak could be related to some type of point defect, but the increase in its height, caused by annealing at room pressure is puzzling. The interpretation of the evolution of the rest of the spectrum is more straightforward. The simultaneous increase in the absorption around 3430 cm^{-1} and decrease in the region between 3400 and 2900 cm^{-1} corresponds to the replacement of the asymmetric broad band (Fig. 12) by the symmetric band of molecular water centered on 3430 cm^{-1} (Mackwell and Paterson, 1985). This result shows that even if H$_2$O molecules occur in the overpressurized tiny
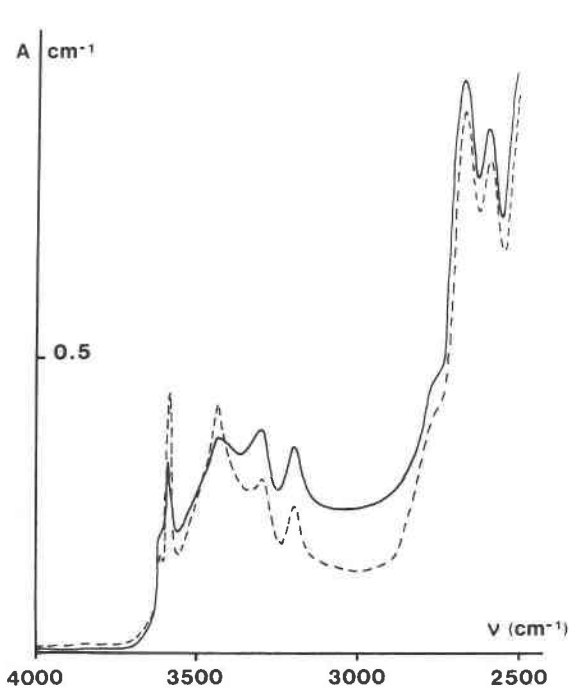

Fig. 9. IR spectra for Bell Telephone sample with a water content 200 atomic ppm, before (solid line) and after (dotted line) annealing for 90 min at 700 °C and ambient pressure.
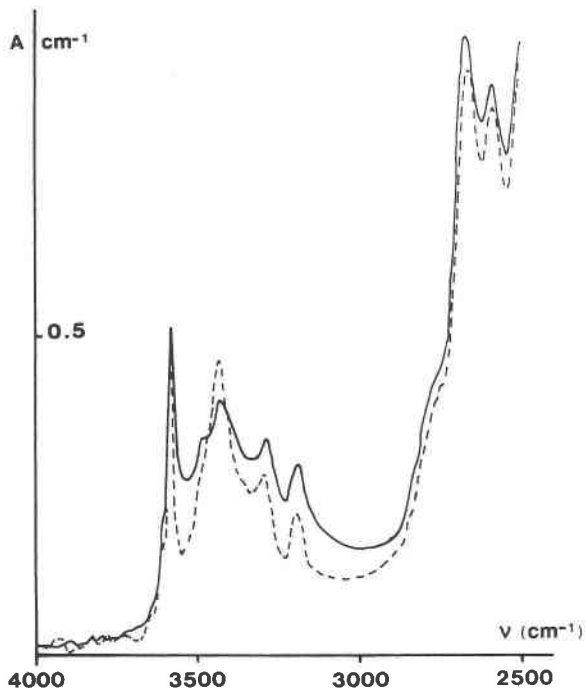

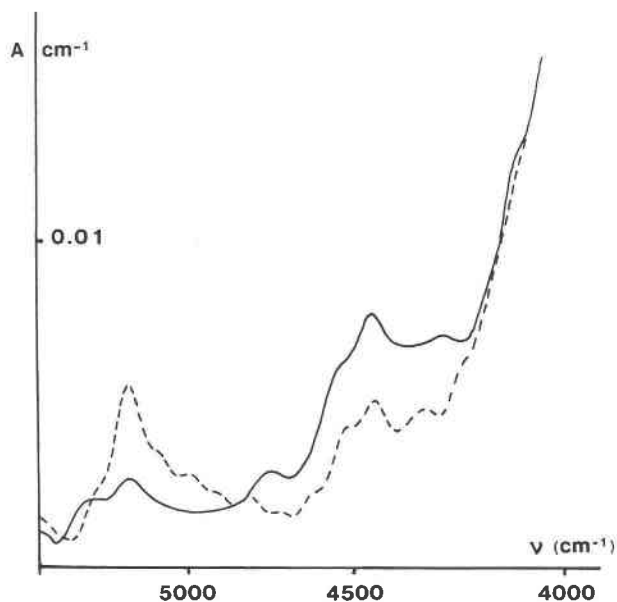Fig. 10. IR spectra for SICN 229 before (solid line) and after (dotted line) annealing for 120 min at 700 C° and ambient pressure.

Fig. 11. NIR spectra for SICN 140 before (solid line) and after (dotted line) annealing for 1 week at 500 °C and ambient pressure.

Fig. 13. NIR spectra for berlinite AlPO$_4$ before (solid line) and after (dotted line) annealing for 14 h at 315 C° and ambient pressure.

bubbles, they are not necessarily part of a fluid phase; the infrared signature is different from that of liquid H$_2$O, and moreover, Aines and Rossman (1984) have shown that IR spectra recorded at low temperatures do not show the presence of ice. These features should be called clusters or aggregates rather than fluid inclusions.

It is interesting to compare the evolution of the NIR spectrum given in Figure 11 to that of "wet" berlinite, AlPO$_4$ (Fig. 13). In the latter case, the band corresponding to water point defects never is lost after annealing, al-
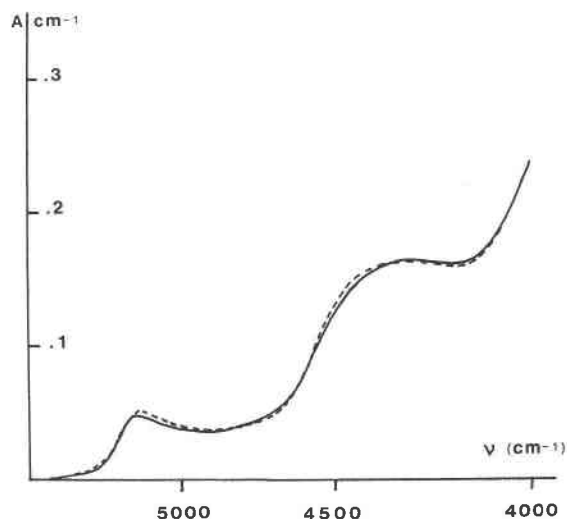
though experiments have been continued until crystals became milky. TEM investigations (Boulogne et al., 1988) clearly show that the water precipitates (bubbles) grow by a mechanism of Oswald ripening (growth of the larger bubbles at the expense of the smaller ones). We interpret this latter result as showing that the water point defects of berlinite (which are related to the absorption band centered on 4500 cm^{-1}) occur essentially in the form of immobile OH associated with impurities with a different valence [probably antisites (Al)$_P$], a situation that compares to that of OH associated with substitutional (Al)$_{Si}$ impurities in quartz.

POLARIZED INFRARED SPECTROSCOPY

As noted above, conventional IR spectroscopy does not provide complete characterization of the mode of incorporation of water in quartz. More information about water speciation is derived from NIR spectroscopy, which can distinguish water molecules from point defects. The fundamental question that remains to be answered is, What is the structure of these point defects? Data indicating the orientation of OH bonds can be obtained from study of the pleochroic behavior of the NIR bands. This method has been applied successfully to the characterization of OH groups in olivine, danburite, and labradorite (Beran and Putnis, 1983; Beran, 1987). We have used this technique to study the orientations of the OH bonds of the water point defects in quartz. We have chosen the crystal SICN 140 (which has the greatest water content of those containing only point defects) and studied the NIR absorption band that is centered on 4500 cm^{-1}. It is clear that, for such experiments, the relative orientation of the beam and the crystal axes (and of course the OH dipoles) is critical. However, in our case, because of the very low absorbance, thick crystals had to be used; adequate absorption could be obtained only with the beam parallel to [10$\bar{1}$0] (the studied crystal was cut in two piec-
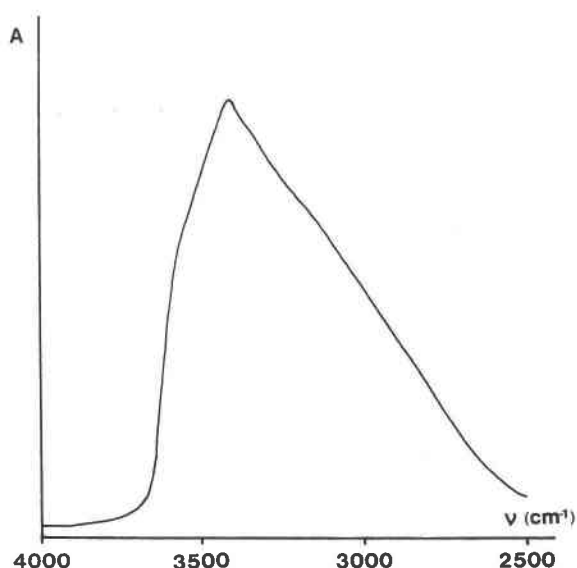

Fig. 12. IR broad absorption band of water in quartz (Bell Telephone crystal). This spectrum has been obtained by subtracting two spectra recorded in regions with a slight difference in water content.
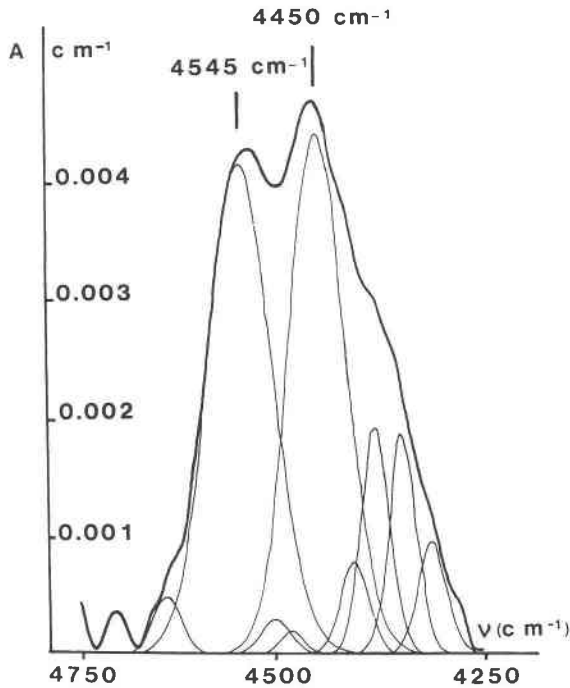
Fig. 14. NIR absorption band of the water point defects for SICN 140. The base line is subtracted. A deconvolution of peaks with Gaussian profiles has tentatively been carried out.
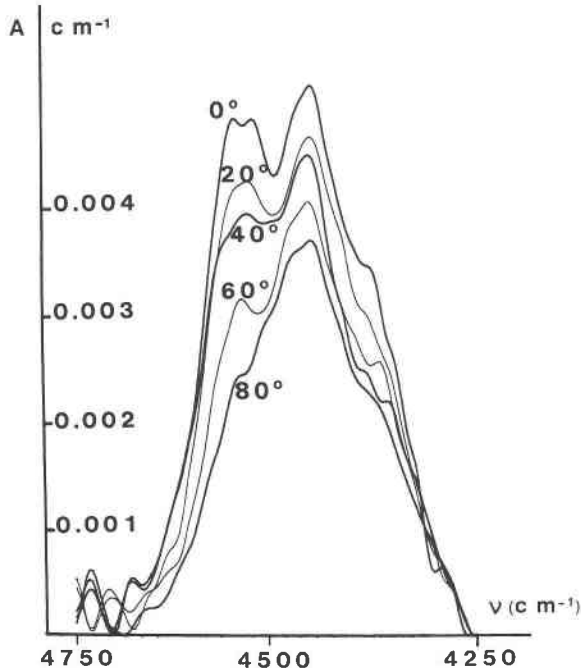

Fig. 15. NIR absorption band of the water point defects for SICN 140 with the beam normal to (10$\bar{1}$0), showing variation of absorbance with the polarization orientation. The angles between the crystal direction **a** and the electric field vector are indicated.
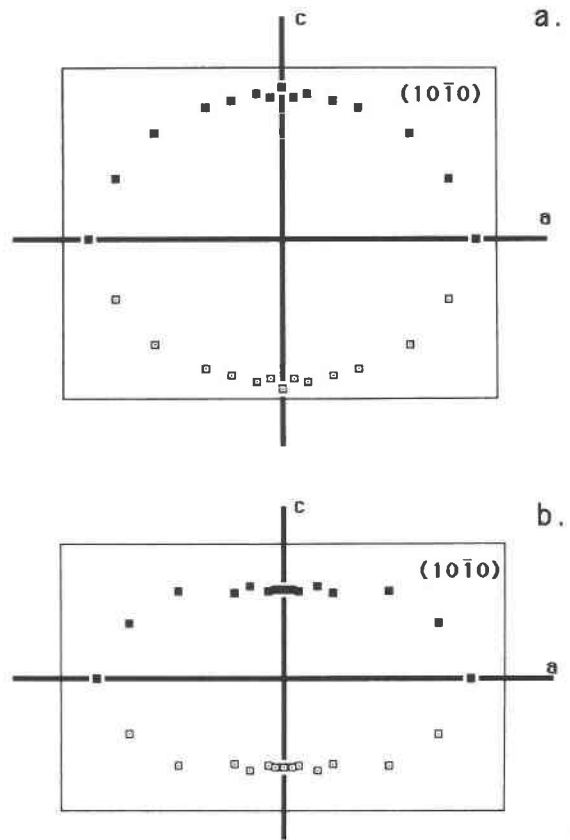

Fig. 16. OH absorbances of the two major peaks of the NIR absorption band. (a) Peak located at 4450 cm^{-1} and (b) peak located at 4545 cm^{-1}. The filled squares are derived from IR measurements. Open squares are derived from observed data from symmetry considerations.

es along its long dimension and the pieces stacked parallel to the beam direction, in order to obtain a total absorption length of 18 cm).

The spectral range corresponding to the absorption band for point defects, after subtraction of the base line, is shown in Figure 14. Point defects with a well-defined structure should give rise to sharp absorption peaks rather than such a relatively broad band; we assumed that this band actually results from the convolution of several sharper peaks and have tried to deconvolute them by assuming they all have Gaussian profiles (Fig. 14). Such a mathematical treatment gives rise to a complex structure with two main peaks and at least eight smaller ones. We have studied in detail the variation of the two mean peaks with the polarization orientation (Figs. 15 and 16). For polarizations in the (10$\bar{1}$0) plane, these peaks are always present, but an anisotropic effect is clearly detected. Unfortunately, the absence of complete extinction prevents the unambiguous determination of the OH dipole orientations. At this time it is not possible to investigate other polarization directions. Nevertheless, our results are consistent with the model of substitutional $(4H)_{Si}$ defects that could give rise to 12 directions for the OH dipoles.

CONCLUSIONS

1. Water-related point defects and H_2O molecules in aggregates (the overpressurized features observed by TEM) are shown to be the prominent sources of water in "wet" synthetic quartz. Unfortunately both species have qualitatively the same infrared signature in the 3-μm range.

2. Generally the incorporation of H_2O molecules in the form of tiny bubbles is favored by growth in impure (doped) nutrients. Very high water contents can be reached in such cases. Al represents a special situation; indeed, when added to the nutrient, Al favors the incorporation of large amounts of water point defects. However, such point defects are the well-known Al-OH compensated defects and are not believed to play a role in hydrolytic weakening. The situation of Al in doped quartz thus compares to those of berlinite $AlPO_4$ and "wet" natural amethyst.

3. The evolution of the microstructure during annealing has been studied by IR and NIR spectroscopy. In NIR spectra, the intensity of the absorption band of point defects centered on 4500 cm^{-1} decreases, whereas that of the absorption band of water molecules increases. The defects responsible for the absorption band centered on 4500 cm^{-1} can thus diffuse and precipitate as water molecules. In IR spectra, the so-called broad band is partially replaced during annealing by the absorption band of H_2O. The water molecules in the aggregates become a macroscopic fluid phase (in larger bubbles).

4. The pleochroism of the absorption band caused by point defects centered on 4500 cm^{-1} has been investigated for polarization in (10$\bar{1}$0). The structure of this absorption band, and thus of the related defects, appears to be complex. Unfortunately, unambiguous determination of the OH dipole orientations was not possible. However, it can be stated that our observations are consistent with the hypothesis of $(4H)_{Si}$ defects. More spectroscopic investigations (nuclear magnetic resonance, electron spin resonance, etc.) are obviously necessary to identify the exact structure of these water-related defects.

ACKNOWLEDGMENTS

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