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Infrared Study of Hydrogen Concentration in Brazilian Quartz

J. A. Medeiros, R. S. Katiyar,* and M. A. F. Scarparo

*Instituto de Física, UNICAMP, 13.100 Campinas, SP, Brazil; and *Department of Physics, University of Puerto Rico, San Juan, PR 00931*

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Infrared transmission spectroscopy is used to determine the amount of hydrogen in several kinds of Brazilian α-quartz. The experiments on the crystallographically oriented samples were used for the first time to verify the applicability of Paterson's formula (M. S. Paterson, *Bull. Mineral.* 105, 20, 1982) using the appropriate orientational factors for polarized and unpolarized radiations. The use of crystallographically oriented samples also allowed us to determine the average preferential direction of the OH dipoles which make an angle of 71° with respect to the optic axis. The hydrogen concentration in the 1st-quality layer of Brazilian quartz was found to be below 70 ppm. © 1994 Academic Press, Inc.

1. INTRODUCTION

The measurement of the absorption coefficient in the vicinity of the 3-μm region is considered to be important for optical transmission in the near infrared, such as for telecommunication with quartz glass fibers. One of the most common impurities found in natural α-quartz is hydrogen. Hydrogen strongly bonds with the oxygen of quartz and thus induces strong absorption in the infrared regions of technological importance, such as optical transmission in the near infrared for telecommunication purposes. The O–H stretching vibrations are known to occur in the region of about 3 μm and can serve as the basis for the quantitative determination of hydrogen in materials using infrared absorption spectroscopy. Since the intensities of the absorption bands depend upon the orientation of the O–H bonds, it is possible to extract information concerning their orientation utilizing crystallography oriented samples. The most common expression used to determine H concentration in quartz was given by Paterson (1). He also described a method for determining the average preferential direction for the OH dipoles using different anisotropic situations. Employing his expressions, the orientational factors and hydrogen concentrations for different kinds of Brazilian natural quartz can be determined. The optical spectrum of a quartz crystal, free from all defects and impurities, is characterized by a highly transparent region extending from the vicinity of the electronic absorption band at about 6900 cm^{-1} to about 3000 cm^{-1}, below which there exist strong secondary absorption bands originating from overtones and from the crystal lattice frequencies. Moreover, the hydrothermal condition of quartz introduces changes in the absorption spectrum in its transparent regions (2, 3) due to impurities which modify its physical properties.

A complex absorption spectrum in the near-infrared region extending to about 3000 cm^{-1} has been studied by numerous authors (4, 6), and a detailed study of the absorption bands was carried out by Kats (6). He showed that these absorption bands are due to vibrations of OH groups associated with various types of lattice defects. Since most of the absorption bands around 3000 cm^{-1} are due to vibrations of OH groups, the infrared spectroscopy is the most appropriate tool for the quantitative determination of H impurities. Using Brazil as a large source of different types and qualities of quartz, the current paper deals with a comparative study of several of them using infrared spectroscopy, taking into account the isotropic and anisotropic behavior of the samples with different OH distributions and orientations.

2. EXPERIMENTAL PROCEDURE

We used different quartz samples of natural gem rocks; most of them were in thin plate forms identified commercially as 1st, 2nd, 3rd, 4th, and mixed (full of optical defects) qualities. All of the samples were obtained from two quartz mines in the State of Minas Gerais, known as Limoeiro and Ribibiu. The 1st plate-like quartz samples have been considered to be high-quality crystals suitable for electronic purposes. The mixed plate-like crystals are full of optical defects and twins. The 3rd and 4th plate-like crystals have been used as raw materials to produce synthetic quartz.

The crystals under investigation were cut from the 1st-quality quartz and oriented along the X, Y, and Z axes by X-ray diffraction techniques. Additionally, we prepared a 1st-quality large sample with approximate dimensions of $12 \times 7 \times 1$ cm. This sample was obtained from a mine in the Bahia State. Infrared absorption spectra were recorded at room temperature between 4000 and 2500 cm^{-1},

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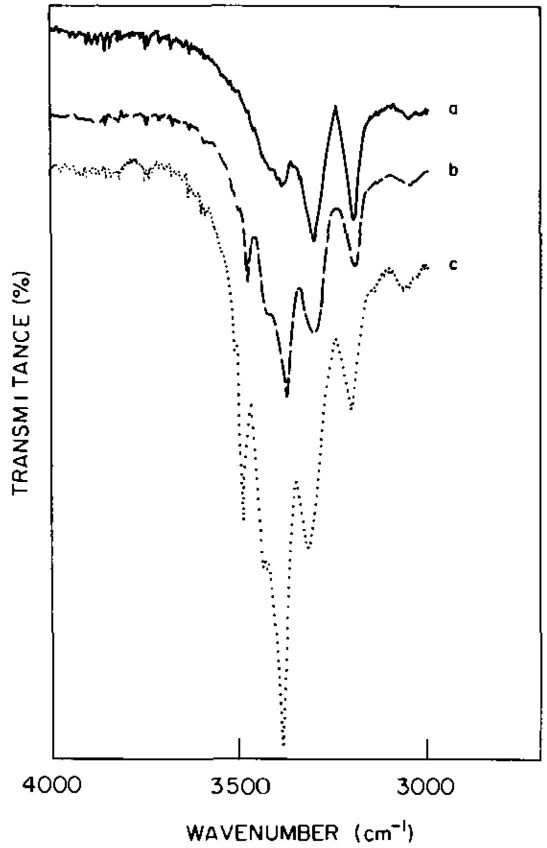

FIG. 1. Transmission spectra of 1st-quality α-quartz crystals with (a) nonpolarized radiation incident along the *Z*-axis, (b) polarized radiation ($E\|C$) incident along the *X*-axis; and (c) polarized radiation ($E\|C$) incident along the *Z*-axis.

using a double-beam Perkin–Elmer Spectrophotometer, Model PE-180. Both polarized and nonpolarized incident radiations were used to record the spectra for all possible orientations of the samples, and few typical absorption spectra for an oriented 1st-quality sample using both polarized and unpolarized radiations are shown in Fig. 1.

3. RESULTS AND DISCUSSION

3.1. Determination of H^+ Concentration in a Crystallographically Oriented Sample

The quantitative determination of H in α-quartz can be obtained by using the Beer–Lambert–Bouger expression, from which the hydrogen concentration can be derived as

$$C = \frac{\int K(\nu)\, d\nu}{\int \varepsilon(\nu)\, d\nu}, \qquad [1]$$

TABLE 1
H Concentration Assuming Isotropic Distribution of OH Dipoles in Quartz

Incidence direction	Nature of polarization	Orientation factor (γ)	Concentration of H (ppm)
X	Unpolarized	$\frac{1}{3}$	62
Y	Unpolarized	$\frac{1}{3}$	59
Z	Unpolarized	$\frac{1}{3}$	101
X	$\|Z$	$\frac{1}{3}$	25
Y	$\|Z$	$\frac{1}{3}$	23
X	$\perp Z$	$\frac{1}{3}$	96
Y	$\perp Z$	$\frac{1}{3}$	98
Z	$\|X$	$\frac{1}{3}$	99
Z	$\|Y$	$\frac{1}{3}$	102

where K is the coefficient of absorption and ε is the molar absorption constant that is characteristic of the material and ν is the radiation frequency.

Following Paterson (1), the absorption spectra due to OH vibrations in quartz in the region of 3 μm can be used as the basis for the computation of H concentration. Taking into account the anisotropy factor γ, for H concentration he obtained the expression

$$C = \frac{22{,}600}{\gamma \cdot 150} \int \frac{K(\nu)\, d\nu}{3780 - \nu}\, H/10^6 Si(ppm), \qquad [2]$$

where

$$K(\nu) = \frac{1}{x} \log \frac{1}{T(\nu)},$$

with x being the thickness of the sample, T the transmittance at the frequency ν, and γ the anisotropic factor.

In order to verify the applicability of the above equations we have computed H concentration for a crystallographically oriented sample assuming isotropic distribution of H impurities for both nonpolarized and polarized radiations. The results of the analysis are listed in Table 1. According to Paterson, if OH distribution is isotropic within the sample then the resulting H concentration in the sample should be independent of the direction and the polarization of the incident radiation. The orientation factor in all such cases was determined to be $\frac{1}{3}$. The results of the analysis lead to significantly different H concentrations for the same small sample. This indicates that the hypothesis of the existence of an isotropic distribution of OH dipoles in the crystal is not valid.

The large differences in the computed values for H concentrations for incident radiation along the *Z*-axis and perpendicular to the *Z* direction are indicative of highly anisotropic behavior in the distribution of the orientation of the OH dipoles, and therefore different orientation factors should be used for different geometries in order to determine the H concentration in oriented samples. We still, however, have to assume that there exists an average preferential direction for the OH dipoles making an angle, say α, with respect to symmetry axis Z (optic axis). The anisotropic factor can then be evaluated in each case following Paterson's analysis, according to which if the incident radiation is not polarized then the anisotropic factor is $\frac{1}{2}\sin\alpha$ or $\frac{1}{2}\cos\alpha + \frac{1}{4}\sin\alpha$, depending upon whether the incident radiation is $\|Z$ or $\perp Z$, respectively, to the crystal axis. On the other hand, for a polarized radiation with polarization $\perp Z$ axis, the anisotropic factor is $\cos^2\alpha$ irrespective of the direction of the incident radiation. Moreover, for a radiation incident $\perp Z$-axis, the anisotropic factor is always $\frac{1}{2}\sin^2\alpha$ irrespective of the direction of polarization, and the latter value also applies for the anisotropic factor in the situation where the incident radiation is polarized $\perp Z$ and is incident $\perp Z$.

Using the above anisotropic factors and formula [2] for determining the H concentration, we have reevaluated all nine experimentally studied cases discussed earlier, for an oriented sample, imposing the requirement that the resulting H concentration be the same. This led to a unique value of α approximately equal to 71°. The analysis also confirms the validity of assuming the existence of an average preferential direction for OH dipoles in quartz and the applicability of the Paterson's equations. These results are summarized in Table 2.

From the above discussion it is evident that once the preferential direction for OH dipoles is determined, in a quartz uniaxial crystal a single infrared absorption spectrum in the 3-μm region should suffice for evaluating the H concentration in it.

TABLE 2

Results of H Concentration Considering Anisotropic Distribution of OH Dipoles with Average Preferential Direction α with Respect to the Optic Axis of the Quartz Crystal

Incidence direction	Polarization	Anisotropy factor (Paterson's formula)	Concentration of H (ppm)
X	Unpolarized	0.28	73
Y	Unpolarized	0.28	70
Z	Unpolarized	0.44	76
X	$\|Z$	0.10	81
Y	$\|Z$	0.10	75
X	$\perp Z$	0.44	69
Y	$\perp Z$	0.44	73
Z	$\|X$	0.44	74
Z	$\|Y$	0.44	76

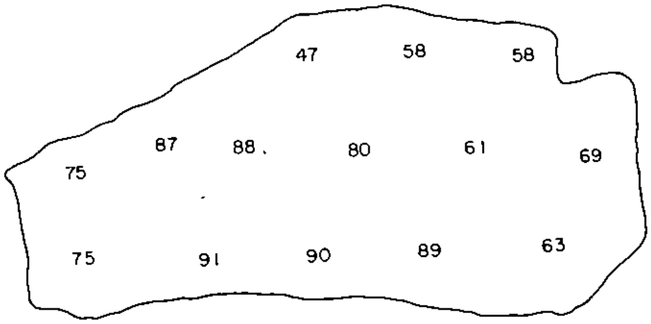

FIG. 2. Mapping of H concentration (in ppm) in a typical 1st-quality natural quartz crystal plate obtained from a mine in the Bahia State of Brazil.

3.2. Local Variation of H Concentration in a Natural Quartz Plate

A commercial 1st-quality quartz plate with dimensions of 12 × 7 × 1 cm was obtained from the quartz mine in the Bahia State of Brazil, and it was selected for studying the local variation of H concentrations as a function of position. Several experimental points were chosen about 2 cm apart from each other, and spectra were recorded at room temperature with nonpolarized infrared radiation. Figure 2 shows the results of the analysis of H concentrations (ppm/10^6 Si) from point to point, the minimum being 41 ppm and the maximum 91 ppm. That means a variation factor on the order of 2 in H concentration in the quartz piece measuring about 12 cm long and 7 cm wide.

It is evident from the mapping results that the H concentration is quite irregular even in the single piece of the 1st-quality gem rock. The variation in the H concentration, however, is much smaller than that reported by Chakraborty and Lehmann (7), who found a variation of 4 to 114 ppm in a quartz piece from the Alps of approximately half the size of ours.

3.3. H Concentration in 1st, 2nd, 3rd, and Mixed Qualities of Natural Quartz

In order to make a comparative study among samples of different classifications we selected a large number of each of them, and their infrared absorption spectra were recorded at room temperature using nonpolarized infrared radiation. Table 3 lists the results for different qualities of samples. It may be noted that in the 1st-quality samples from both the Limoeiro and Ribibiu mines in the State of Minas Gerais the H concentration was found to be less than 70 ppm in all of the samples. The 1st quality optically defective samples (known as mixed plates) also had H concentrations below 95 ppm. The second-quality samples normally had H concentrations in the range of 100 to 500 ppm, whereas the third-quality samples showed H

TABLE 3
H Concentration in Several Different Quality Samples of Brazilian α-Quartz Crystals

Commercial qualities	Samples	H concentration (ppm)
1st quality	L1L-1	32
	L1L-2	36
	L1L-3	42
	L1L-4	57
	L1L-5	65
1st-quality layer	L1R-1	21
	L1R-2	39
	L1R-3	54
	L1R-4	60
Mixed layer	LML-1	18
	LML-2	94
	LMR-1	42
	LMR-2	85
2nd-quality layer	L-2-L	338
	L-2-R	117
3rd-quality layer	L-3-L	1250
	L-3-R	5452

concentrations well above these limits, generally above 1000 ppm.

4. CONCLUSION

The infrared absorption studies on the crystallographically oriented samples showed that the distribution of the OH dipoles, which are responsible for the strong infrared absorption bands around the 3-μm region, is indeed highly anisotropic. However, these dipoles are approximately oriented at about 71° with respect to the optic axis of the crystal. Paterson's formula seems to be adequate for the quantitative determination of H concentrations as well as for determining the average preferential direction of OH dipoles in the crystallographically oriented quartz samples. Using expressions for the anisotropic factor, the H concentration was found to be the same in all nine different geometrical arrangements for the infrared absorption studies in an oriented sample of quartz. Paterson's formula with the anisotropic factor, therefore, represents a substantial improvement over the existing calculations by others (8–10).

The H concentration in the 1st-quality and the optically defective gem rocks from Limoeiro and Ribibiu mines in Brazil was found to be below 70 ppm. In 2nd- and 3rd-quality samples the H concentration was found to be quite higher, making them unsuitable for optical communication. However, they can be utilized as raw materials to produce synthetic quartz.

Local variation of H concentration in a quartz sample of 1st-quality gem rock (from Bahia) is about 47–91 ppm in a plate of about 12 × 7 cm.

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